PREFACE

In a bid to standardise higher education in the country, the University Grants Commission (UGC) has introduced Choice Based Credit System (CBCS) based on five types of courses viz. *core, discipline specific generic elective, ability* and *skill enhancement* for graduate students of all programmes at Honours level. This brings in the semester pattern, which finds efficacy in sync with credit system, credit transfer, comprehensive continuous assessments and a graded pattern of evaluation. The objective is to offer learners ample flexibility to choose from a wide gamut of courses, as also to provide them lateral mobility between various educational institutions in the country where they can carry acquired credits. I am happy to note that the University has been accredited by NAAC with grade 'A'.

UGC (Open and Distance Learning Programmes and Online Learning Programmes) Regulations, 2020 have mandated compliance with CBCS for U.G. programmes for all the HEIs in this mode. Welcoming this paradigm shift in higher education, Netaji Subhas Open University (NSOU) has resolved to adopt CBCS from the academic session 2021-22 at the Under Graduate Degree Programme level. The present syllabus, framed in the spirit of syllabi recommended by UGC, lays due stress on all aspects envisaged in the curricular framework of the apex body on higher education. It will be imparted to learners over the *six* semesters of the Programme.

Self Learning Materials (SLMs) are the mainstay of Student Support Services (SSS) of an Open University. From a logistic point of view, NSOU has embarked upon CBCS presently with SLMs in English / Bengali. Eventually, the English version SLMs will be translated into Bengali too, for the benefit of learners. As always, all of our teaching faculties contributed in this process. In addition to this we have also requisitioned the services of best academics in each domain in preparation of the new SLMs. I am sure they will be of commendable academic support. We look forward to proactive feedback from all stakeholders who will participate in the teaching-learning based on these study materials. It has been a very challenging task well executed, and I congratulate all concerned in the preparation of these SLMs.

I wish the venture a grand success.

Professor (Dr.) Subha Sankar Sarkar

Vice-Chancellor

Netaji Subhas Open University

Under Graduate Degree Programme

Choice Based Credit System (CBCS)

Subject: Honours in Chemistry (HCH)

Course : Practical Paper - II

Course Code - CC-CH-02

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Module-1

Module-2

Basic Laboratory Knowledge

LABORATORY SAFETY AND FIRST AID

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

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

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

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

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

v) Wash your apparatus thoroughly with a washing powder.

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

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

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

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

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

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

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

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

Laboratory First-Aid:

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

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

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

Bromine :Treat with (2M) 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:

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:

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

3. Preparation of Some Common Indicators:

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

4. Equivalent Weight of Some Common Reagents:

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

Module - I

(Inorganic Chemistry)

Unit-1 □ Estimation of Ions

Structure

1.1 Objectives

In this Unit a learner will acquire the laboratory based knowledge on:

- Different types of standard substances
- Equivalent weights of oxidants and reductants
- Different types of strength of a solution
- Theory, principle and procedure for the estimation of various ions in the mixtures using redox titration

1.2 Introduction

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.

1.2.1 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.

1.2.2 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.

1.2.3 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 110^0 - 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.

Oxiditnetry 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.

1.2.4 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.

1.2.5 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.

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:

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

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

$$= \frac{294.18}{6} = 49.03.$$

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

$H_2C_2O_4$ acts as a reductant:

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

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

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

1.2.6 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].

1.3 Experiment-1: Estimation of Fe(II) and Fe(III) in a given mixture using $K_2Cr_2O_7$ solution

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 ppt appears. This ensures the completeness of the reduction.

$$2Fe^{+3} + Sn^{+2} \rightleftharpoons 2Fe^{+3} + Sn^{+4}$$

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

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+}

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

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

or 1/6 mole $Cr_2O_7^{2-}$ ≡ 1 mole Fe^{2+} ≡ 1 Equivalent

Hence, 1 g 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

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

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)

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 Ba-diphenylaminesulphonate 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 $SnCl_2$ 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 ppt. 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 Ba-diphenylaminesulphonate 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.

Experimental Results

Table1: 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					

Table2: Estimation of total iron (Fe^{2+}+ Fe^{3+}) after reduction with $SnCl_2$

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					

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

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

≡ (0.055847 × y × S × 40)g/L of total Fe

≡ B g/L

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

∴ Amount of Fe^{3+} ion in the given mixture = (B-A) g/L

1.4 Experiment-2: Estimation of Fe(III) and Cu(II) in a given mixture using $K_2Cr_2O_7$ solution

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+} can not 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.

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

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

$\therefore$ 2 moles $Cu^{2+} \equiv$ 1 mole $I_2 \equiv$ 2 moles $S_2O_3^{2-}$

$\therefore$ 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.

$$2Fe^{+3} + Sn^{+2} \rightleftharpoons 2Fe^{+3} + Sn^{+4}$$

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

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

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

Or, 1000 ml 1 (N) $K_2Cr_2O_7$ solution $\equiv$ 55.847 g of Fe

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)

Procedure

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

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

Pipette out 25 mL 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 ppt. 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 Ba-diphenylaminesulphonate 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.

Experimental Results

Table1: 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
			1.225	= (w_1–w_2)/1.225 (N/10)

Table2: 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 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					

Table3: Estimation of Cu^{2+}

No. of Titrations	Volume of diluted mixture 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					

Table4: Estimation of Fe^{3+}

No. of Titrations	Volume of diluted mixture 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					

Calculation

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 = $\frac{\text{Volume of mixture taken} \times S_1}{\text{volume of } Na_2S_2O_3 \text{ solution required}}$

= 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 × x × S_2)g of of Cu

≡ (0.063546 × x × S_2 × 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 ≡ y mL S_1 (N) $K_2Cr_2O_7$ solution

≡ y S_1 mL 1(N) $K_2Cr_2O_7$ solution

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

∴ y S_1 mL 1(N) $K_2Cr_2O_7$ solution ≡ (0.055847 × y × S_1)g of Fe

≡ (0.055847 × y × S_1 × 40)g/L of Fe

≡ B g/L

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

1.5 Experiment-3: Estimation of Cr(VI) and Mn(II) in a given mixture using $K_2Cr_2O_7$ solution

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.

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

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

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

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

$$\equiv 17.332 \text{ g of Cr}$$

From the precipitate part Manganese ion is estimated. The precipitate containing MnO_2 is dissolved in measured excess of standard Mohr's salt solution and Mn^{2+} can then be estimated by back titrating with standard $K_2Cr_2O_7$ solution in presence of phosphoric acid using Ba-diphenylaminesulphonate (BDS) as indicator.

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

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

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

$\therefore$ 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 $\times$ 1.01g of Mn^{2+}

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

Chemicals Required

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

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

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

(iv) Sodium peroxide

(v) 5% $KBrO_3$

(vi) Conc H_2SO_4

(vii) Syrupy H_3PO_4

(viii) Whatman No-1 filter paper

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

Procedure

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

(2) Prepare 250 mL of a standard 4 (N/20) $K_2Cr_2O_7$ solution by accurate weighing.

(3) 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 3mL syrupy H_3PO_4 and 3-4 drops of Ba-diphenylaminesulphonate (BDS) indicator. Titrate the solution with the standard $K_2Cr_2O_7$ solution until the colour changes from green to reddish-violet.

(4) 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 ppt. 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

5) 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.

6) 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 Ba-diphenyl amminesuiphonate (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 (1:1) H_2SO_4, 5 ml of syrupy H_3PO_4 and 6-8 drops of Ba-diphenyl amminesuiphonate (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.

Experimental Results

Table1: Preparation of standard 250 mL 4 (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)

Table2: Standardization of Mohr's salt solution Vs (N/20) $K_2Cr_2O_7$ solution

No. of Titrations	Volume of Mohr's salt solution taken in mL	Burette reading of $K_2Cr_2O_7$		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					

Table3: Titration for the Estimation of Chromium ion

No. of Titrations	Volume of solution 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					

Table4: Titration for the Estimation of Manganese ion

No. of Titrations	Volume of stock solution mixture+ measured excess of standard Mohr's salt solution 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					

Calculation

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 ≡ x 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) × S mL 1 (N) $K_2Cr_2O_7$ solution

≡ 10 × (2x-z) × S mL 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

1.6 Experiment-4: Estimation of Fe(III) and Cr(VI) in a given mixture using $K_2Cr_2O_7$ solution

Theory

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

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

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

Or, 1 mole Fe^{2+} ≡ 1/6 mole $Cr_2O_7^{2-}$ ≡ 1/3 mole of Cr ≡ 1 Equivalent

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

≡ 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 Ba-diphenylaminesulphonate as indicator.

$$2Fe^{+3} + Sn^{+2} \equiv 2Fe^{+3} + Sn^{+4}$$

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

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

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

Or, 1000 ml 1 (N) $K_2Cr_2O_7$ solution $\equiv$ 55.847 g of Fe

Chemicals Required

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

(ii) Mohr's salt solution

(iii) Saturated aqueous solution of Barium-diphenylaminesulphonate (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)

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

(c) 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 Ba-diphenylaminesulphonate indicator. Titrate the solution with the standard $K_2Cr_2O_7$ solution until the colour changes from green to reddish- violet.

(d) 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 4 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 Ba-diphenylaminesulphonate indicator. Titrate the solution with the standard $K_2Cr_2O_7$ solution until the colour changes from green to reddish- violet.

(e) Estimation of Fe:

Pipette out 25mL of the above diluted solution to a 500mL conical flask, dilute to 100mL with distilled water, add 1 g 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 ppt. 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 Ba-diphenylaminesulphonate 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.

Experimental Results

Table1: Preparation of standard 250 mL ~ (N/20) $K_2Cr_2O_7$ solution

Initial weight (w_1g)	Final weight (w_2 g)	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)

Table2: Standardization of Mohr's salt solution vs (N/20) $K_2Cr_2O_7$ solution

No. of Titrations	Volume of Mohr's salt solution taken in mL	Burette reading of $K_2Cr_2O_7$		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					

Table3: Back titration for the Estimation of Cr(VI) as $Cr_2O_7^{2-}$

No. of Titrations	Volume of mixture + Mohr's salt solution 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					

Table4: Estimation of Fe^{3+}

No. of Titrations	Volume of diluted stock solution 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					

Calculation

(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 ≡ $10 \times x \times$ S mL (N) $K_2Cr_2O_7$ solution

We have, 1000 mL 1 (N) $K_2Cr_2O_7$ 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

(c) 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

≡ $[(2y-z) \times S]$ mL 1 (N) $K_2Cr_2O_7$ solution

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

≡ $10 \times (2y-z) \times$ S mL 1 (N) $K_2Cr_2O_7$ solution

≡ $10 \times (2y-z) \times$ S mL 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) × S g

1.7 Experiment-5: Estimation of Fe(III) and Mn(II) in a given mixture using $KMnO_4$ solution

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.

$$2Fe^{+3} + Sn^{+2} \rightleftharpoons 2Fe^{+3} + Sn^{+4}$$

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

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

∴ 1 mole MnO_4^- ≡ 5 moles of Fe^{2+}

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

∴ 1000 mL (N) $KMnO_4$ solution ≡ 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.

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

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

∴ 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

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

≡ 10.9876 g of Mn^{2+}

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)

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 ~ (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 l0 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 Fe^{3+} may also be done with Al-foil in 4(N) HCl medium and then the above method is followed.

(e) Estimation of Mn:

Step-1 : 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.

Step-2 : 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 150mL 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.

Experimental Results

Table1: Preparation of 250 mL standard ~ (N/20) oxalic acid solution

Initial weight (w_1 g)	Final weight (w_2 g)	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/10)

Table2: Standardization of $KMnO_4$ 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 $KMnO_4$ required in mL
		Initial	Final		
1					
2					
3					

Table3: Titration for the Estimation of Fe^{3+}

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 $KMnO_4$ required in mL
		Initial	Final		
1					
2					
3					

Table4: Estimation of Mn

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

Calculation

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

ii) Strength of prepared $KMnO_4$ solution

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

$= S_2$ (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 ≡ 55.847 g 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_2 mL (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+}

10 × (2y-z) × S_2 mL 1 (N) $KMnO_4$ solution

≡ 0.0109876 × 10 × (2y-z) × S_2 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+}

1.8 Experiment-6: Estimation of Fe(III) and Ca(II) in a given mixture using $KMnO_4$ solution

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:

$$2Fe^{+3} + Sn^{+2} \rightleftharpoons 2Fe^{+3} + Sn^{+4}$$

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

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

∴ 1 mole MnO_4^- ≡ 5 moles of Fe^{2+}

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

∴ 1000 mL (N) $KMnO_4$ solution ≡ 55.847 g of Fe^{2+}

From the mixture Fe^{3+} is first separated by precipitating it as hydrated ferric oxide, $Fe_2O_3.xH_2O$ and from the filtrate 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

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

Chemicals required

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

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

(c) 5% $HgCl_2$ solution

(d) 15% $SnCl_2$ 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

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

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

(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 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:

Step1: 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) NH_4OH 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).

Step2: 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 $KMnO_4$ solution until pale pink colour persist for 30 seconds.

Experimental Results

Table1: 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 $K_2Cr_2O_7$ solution prepared
			0.7879	= (w_1–w_2)/0.7879 (N/20)

Table2: Standardization of $KMnO_4$ 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 $KMnO_4$ required in mL
		Initial	Final		
1					
2					
3					

Table3: Titration for the Estimation of Fe^{3+}

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

Calculation

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

ii) Strength of prepared $KMnO_4$ solution

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

$= S_2$ (N)

iii) Estimation of Fe^{3+}

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

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

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

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

∴ The total amount of Fe^{3+} ion in the supplied mixture

$= (0.055847 \times 10 \times x \times S_2)$ g

(c) Estimation of Ca^{2+}

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

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

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

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

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

$= (0.02004 \times 10 \times y \times S_2)$ g

1.9 Summary

- Primary standard substances are the substances 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.
- 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.
- 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.
- For the calculation of a titration generally the strength of a solution is expressed in normality (N).
- We have to maintain the conditions such as pH, temperature time of addition of indicator etc. for each titration as the procedure discussed for individual experiments to obtain accurate result.

1.10 Questions

Q1. Why should weights not be lifted with hand?

Ans. This causes error in the weighing because some matter may be transferred from the hand to the weight.

Q2. What is the principle of volumetric analysis?

Ans. In volumetric analysis, the concentration of a solution is determined by allowing a known volume of this to react quantitatively with another solution of known concentration.

Q3. What is titration?

Ans. The process of adding one solution from the burette to another in the titration flask in order to complete the chemical reaction involved, is known as titration.

Q4. What is indicator?

Ans. Indicator is a chemical substance which changes colour at the end point.

Q5. What is end point?

Ans. The stage during titration at which the reaction is just complete is known as the end point of titration.

Q6. What are primary and secondary standard substances?

Ans. See text 1.1.2

Q7. What is a normal solution?

Ans. A normal solution is a solution, a litre of which contains one gm-equivalent of the solute. This is symbolized as 1 N.

Q8. What do you mean by 1.0 M solution?

Ans. A solution containing 1 mole of solute per litre of solution is 1.0 M solution.

Q9. What is the difference between an end point and an equivalence point?

Ans. End point is the point at which the indicator shows a visible change indicating that the reaction has completed. Equivalence point is the point at which stoichiometric amounts of the two reactants have been added. Visible end point may or may not exactly coincide with equivalence point.

Q10. What is Mohr's Salt?

Ans: Ammonium ferrous sulfate or ammonium iron(II) sulfate

Unit-2 □ Complexometric Titration

Structure

2.1 Objectives

At the end of this unit the learner is expected to be able to:

- Define complex formation reactions.
- Differentiate between uni- and polydentate complexing agents.
- Understand the mechanism of complex formation reaction and the methods used for equivalent point detection.
- Realize the effect of pH on the formation of metal ions complexes.
- Distinguish between simple complexes and chelates.
- Know the applications of complex formation reactions in analytical chemistry.
- The importance of EDTA particularly in the determination of water hardness.
- Estimate Ca^{2+} and Mg^{+2} together by complexometry
- Estimate Zn^{2+} and Mg^{+2} together by complexometry

2.2 Introduction

The technique involves titrating metal ions with a complexing agent or chelating agent (Ligand) and is commonly referred to as complexometric titration. This method represents the analytical application of a complexation reaction. In this method, a simple ion is transformed into a complex ion and the equivalence point is determined by using

metal indicators or electrometrically. Various other names such as chilometric titrations, chilometry, chilatometric titrations and EDTA titrations have been used to describe this method. All these terms refer to same analytical method and they have resulted from the use of EDTA (Ethylene diamine tetra acetic acid) and other chilons. These chilons react with metal ions to form a special type of complex known as chelate.

Metal ions in solution are always solvated, i.e. a definite number of solvent molecules are firmly bound to the metal ion. However, these bound solvent molecules are replaced by other solvent molecules or ions during the formation of a metal complex or metal coordination compound. The molecules or ions which displace the solvent molecules are called Ligands. Ligands or complexing agents or chelating agents can be any electron donating entity, which has the ability to bind to the metal ion and produce a complex ion. Few examples of these types of complexometric titration using EDTA will be discussed in this Unit.

2.3 Estimation of Hardness of water

A. Theory

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 pH-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.

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

Blue Wine-red

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

Wine-red Blue

B. Apparatus

i. Burette

ii. Pipette

iii. 250 ml volumetric flask

iv. Conical flask (250 & 500 ml)

C. 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].

D. 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.

Table – 1:

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)

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.

(iii) 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.

E. Experimental Results

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

No. of obs.	Volm. of Zn-acetate (ml)	Burette reading		Volm. of EDTA (ml)	Mean volm. 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.	Volm. of Hard water (ml)	Burette reading		Volm. of EDTA (ml)	Mean volm. of EDTA (ml)
		Initial	Final		
1.	50	0	...	...	
2.	50	...	...	...	V
3.	50	...	...	...	

F. 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, $V \times S = V_1 \times S_1$; $\therefore S_1 = \frac{25 \times W}{0.5488 \times V_1}$ (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) $CaCO_3$

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

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

≡ $V \times y \times 10^{-3}$ 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

2.4 Estimation of Ca (II) and Mg (II) in a mixture

A. Theory

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 $CaCO_3$

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

B. Apparatus

i. Burette
ii. Pipette
iii. 500 ml volumetric flask
iv. 250 ml Conical flask
v. 250 ml beaker
vi. Funnel
vii. Glass rod

C. 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. 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 NH_3 (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

D. 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 :

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.

E. Experimental Results :

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

Table – 1:

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.	Volm. of Zn-acetate (ml)	Burette reading		Volm. of EDTA (ml)	Mean volm. of EDTA (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V
3.	25	...	...	...	

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

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

Table – 4: Estimation of Ca with standard EDTA

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

F. 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 25 ml 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 $\equiv$ 84.31 g $MgCO_3$

$\therefore (V_1 - V_2) \times$ S ml (M) EDTA solution

$\equiv 0.08431 \times (V_1 - V_2) \times$ S g of $MgCO_3$/ 25 ml mixture

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

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 $CaCO_3$

$V_2 \times$ 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 $CaCO_3$

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

= W_1 g of $CaCO_3$

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

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

2.5 Estimation of Zn (II) and Mg (II) in a mixture:

A. Theory

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+}.

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

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

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

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

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

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

$\therefore$ 1 mole 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

B. Apparatus

viii. Burette

ix. Pipette

x. 500 ml volumetric flask

xi. Conical flask (250 & 500 ml)

C. 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 NH_3 (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.

D. 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.

E. 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 (M/100)
W_1	W_2	$W = W_1 - W_2$	W/ 1.0957

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

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

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

No. of obs.	Volm. of supplied mixture + measured excess standard EDTA (ml)	Burette reading		Volm. of Zn-acetate (ml)	Mean volm. of Zn-acetate (ml)
		Initial	Final		
1.	25 + 50	0	...	...	
2.	25 + 50	...	...	...	y
3.	25 + 50	...	...	...	

Table – 4 : Estimation of Mg^{2+}

No. of obs.	Volm. of supplied mixture (ml)	Burette reading		Volm. of Zn-acetate (ml)	Mean volm. of Zn-acetate (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	z
3.	25	...	...	...	

F. 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, $V \times S = V_1 \times S_1$; ∴ Strength of EDTA solution

$$= \frac{x \times W}{1.0957 \times 25} \quad (M/100) = S_1 \text{ (M)}$$

∴ 25 ml S_1 (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

EDTA consumed by 25 ml of (Mg^{2+} + Zn^{2+}) mixture ≡ (2x – y) ml S_2 (M) Zn-acetate solution ≡ (2x – y) x 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 x S_2 ml (M) EDTA solution

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

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

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) × S_2 ml (M) EDTA solution

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

∴ (2x – y - z) x S_2 ml (M) EDTA solution

≡ 0.06538 × (2x – y - z) × S_2 g of Zn^{2+} / 25 ml of the mixture

∴ Amount of Mg^{2+} in the supplied mixture

= 0.06538 × (2x – y - z) × S_2 × 40 g/L

2.6 Summary

- Calcium and magnesium reacts with EDTA to form stable complexes at pH-7 to pH-11.
- The Calcium complex of EDTA is more stable than the Magnesium – EDTA complex.
- 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.
- Ca^{2+} in the mixture can be estimated against standard EDTA solution at pH 12.3 using Calcon or Patton- Reeder's indicator.
- During the estimation of Ca and Mg Calcon or Patton- Reeder's indicator changes the colour from wine - red to blue.
- Estimation of Zn (II) and Mg (II) in a mixture using EDTA solution, standard Zn- acetate solution at pH 10 using Eriochrome Black T (EBT) as indicator.

2.7 Questions

Q1. EDTA is a versatile complexing agent. What are its limitations?

Ans: It is true that EDTA is a versatile complexometric agent and has been extensively exploited for quantitative determinations of the metal ions. However, it cannot be used for the direct analysis of anions or neutral ligands.

Q2. What is chelating ligand?

Ans: see text 3.1

Q3. What is back titration?

Ans: Back titration involves addition of a known excess of Chelating agent (eg. EDTA) to the metal ion then, the excess Chelating agent is titrated with a standard solution of a different metal ion.

Q4. What is masking reagent?

Ans: A substance that decreases the concentration of a free metal ion or ligand by conversion into an essentially unreactive form, thus preventing undesirable chemical reactions that would interfere with the determination is called masking reagent.

Q5. Erichrome black -T used indicator in which type of titrations?

Ans: complexometric titration

Q6. Which indicator is used in the estimation of hardness of water?

Ans: Erichrome black –T

Q7. Which buffer is used in hardness determination?

Ans: Mixture of ammonia and ammonium chloride solutions in water

Q8. What pH is maintained for the estimation of Ca^{2+} and Mg^{2+} ions by titrating with standard EDTA solution?

Ans: pH10

Q9. What is temporary hardness?

Ans: Hardness of water due to presence of carbonates and bicarbonate of Calcium and magnesium is called temporary hardness.

Q10. What is ppm?

Ans: see text 2.1

Q11. Standardisation of EDTA done by which solution?

Ans: standard Zn- acetate solution.

Unit-3 □ Inorganic Preparation

Structure

3.1 Objectives

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.

3.2 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.

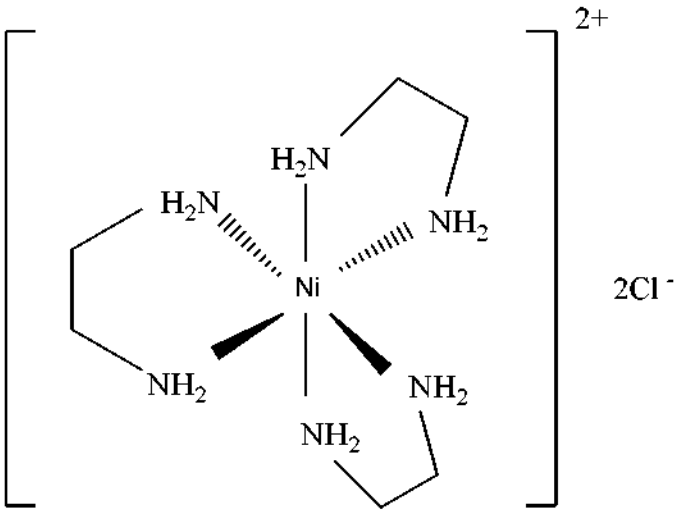
For an example the synthesis reaction of tris(ethylenediamine)nickel(II)chloride is represented by the balanced equation:

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

"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

3.2.1 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.

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

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

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

3.2.2 General discussion for the inorganic preparation of complex compounds

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

- Read the procedure in details before performing the reaction
- Check the availability of the reagents and instruments required for the reaction in your laboratory
- Check if there is any possibility of accident, poisonous gas evolution during the reaction or during the handling of chemicals.
- After completing the reaction, product should be collected and dried as described the procedure. Note the amount of the dry product obtained.
- Calculate the percentage yield of the reaction

3.3 Experiment – 1: Preparation of Tris(ethylenediamine)-nickel(II) chloride $Ni(en)_3Cl_2$

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 $Ni(en)_3Cl_2$	Theoretical $Ni(en)_3Cl_2$ obtained	percentage yield of product

3.4 Experiment – 2: Preparation of Ferrous ammonium sulphate (Mohr's salt); $FeSO_4(NH_4)_2SO_4.6H_2O$

Principle

When a mixture containing equimolar proportions of ferrous sulphate ($FeSO_4$) 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

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

Principle

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

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

Chemicals required:

(a) Oxalic acid, $H_2C_2O_4.2\ H_2O$: 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 $K_3[Cr(C_2O_4)_3].3H_2O$ obtained	percentage yield of product

3.6 Experiment – 4 : Preparation of Tetraamminecarbonatocobalt(III) nitrate; $[Co(CO_3)(NH_3)_4]NO_3$

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) $Co(NO_3)_2.6H_2O$: l0g

(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 l0g of $Co(NO_3)_2.6H_2O$ in l0mL of warm water and add to it a mixture of 20g of $(NH_4)_2CO_3$ in l00mL 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 $[Co(CO_3)(NH_3)_4]\ NO_3$ obtained	percentage yield of product

3.7 Experiment – 5 : Preparation of Potassiumbis (oxalato) cuprate(II)-dihydrate $K_2[Cu(C_2O_4)_2].\ 2H_2O$

Principle:

Potassium bis(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) +5 H_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

3.8 Summary

- Tris (ethylenediamine) nickel(II) chloride is prepared by adding ethylenediamine in small portions to aqueous solution of nickel chloride.
- Tris (ethylenediamine) nickel(II) chloride is water-soluble and your product will be lost if you wash it with water.
- Mohr's salt is a double salt and crystallized from the equimolar mixture of ferrous sulphate and ammonium sulphate in solution.

- Potassiumtrioxalatochromate (III) trihydrate is made by adding potassium dichromate in small portions to a hot solution of oxalic acid.
- Carbonatotetraamine cobalt (III) nitrate is violet crystalline substances.
- Potassiumbis(oxalato) cuprate(II) dihydrate is made by adding copper(II) sulphate solution in small portions to a hot solution of potassium oxalate.

3.9 Questions

Q1. Define the term 'crystallisation'.

Ans: The substances when present in well-defined geometrical shapes are called crystals. These are formed when a hot saturated solution of the salt is allowed to cool slowly and undisturbed. The process of obtaining crystals is termed as crystallisation.

Q2. What is the formula for calculating the percentage yield?

Ans: see text 3.1.2

Q3. What is meant by equimolar proportions?

Ans: Proportion of the substances in the ratio of their molecular masses, i.e. 1: 1 mole ratio.

Q4. In the preparation of Mohr's salt can concentrated H_2SO_4 be used in place of dilute H_2SO_4?

Ans: No, because it would oxidize ferrous ions to ferric ions.

Q5. What is the difference between a complex and a double salt?

Ans: In complex salt, the properties of all individual ions of the constituent salts may not be exhibited. Whereas in double salts properties of the ions of the constituent salts are exhibited in solution.

Q6. What are chelates?

Ans: Multidentate ligands are known as chelates.

Q7. Why does the compound, Potassiumbis(oxalato)cuprate(II)-dihydrate, not give tests for cupper ions ?

Ans: Because it contains Cu(II) as complex ion.

Q8. What is the coordination number of iron is Tris(ethylenediamine)nickel(II) chloride ?

Ans: Six

Q9. What is mother liquor?

Ans: The liquid left behind after the separation of crystals from a saturated solution is known as mother liquor. It contains soluble impurities.

Q10. What is the principle for the preparation of Potassiumtrioxalatochromate (III) trihydrate?

Ans: see text 3.4

Module - II

(Organic Chemistry)

Unit-4 □ Qualitative Analysis of Single Organic Compounds

Structure

4.1 Objectives

At the end of this unit the learner is expected to be able to:

- Identify the physical characteristics of an organic compound.
- Perform solubility tests in different solvent to find out the nature of the functional groups present in an organic compound
- Perform the Lassaigne's Test for the detection of special elements such as N, S and halogens present in organic compound
- Detect the functional group(s) present in unknown organic compound
- Identify the unknown compound with the Consultation of Literature data.
- Prepare derivatives of the functional group and its M.P. determination .
- Know the chemical reactions involve in the organic qualitative analysis of an unknown organic coumpound.

4.2 Introduction

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

(i) Qualitative Organic Analysis.

(ii) Quantitative Organic Analysis.

(iii) Organic Preparations.

We have learned procedures for the Organic Preparation in CC 1. Remaining two aspects will be discussed in this subsequent chapters.

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.

Basic Concepts

A mixture of inorganic compounds can be qualitatively analysed because most of the inorganic compounds ionise to cations and anions and each of them can be identified and probable compositions can be determined by their solubilities, colours and special test, etc. Organic reactions are mostly non-ionic in character and the majority of tests are influenced by the presence of other substances. Moreover, a mixture of organic substances with the same functional groups cannot be separated by chemical methods and common physical methods are inadequate for their separation. That is why, a mixture of organic substances can not be used for direct detection of any one of the constituents and the mixture must be separated and purified into their individual components before analysis. The methods of purification are beyond the scope of this book. However, the purity of a compound can be tested by determination of the boiling points and the melting points for liquids and solids respectively. The sharp transition temperatures (boiling points and melting points) indicate the pure compound. If no sharp transition temperatures are obtained, then the liquids should be fractionally distilled and the solids should be recrystallised to get the pure substance.

The idendification or detection of organic compounds and representation in the notebook may be based on the following procedures and guideline.

4.3 Physical characteristics

(i) State:

(ii) Odour:

(iii) Colour:

(iv) M.P = ... ^{0}C

(v) 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	×	✓	×	-	-	S_1	
3	×	×	✓	×	-	S_2	
4	×	×	✓	✓	-	S_3	
5	✓	✓	✓	✓	-	S_4	
6	×	×	×	-	✓	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 othe 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	Nutral in nature; Amide, Anilide, Nitro, Aldehyde, Ketone and Ester

4.4 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. burner	2. Rapid decolourisation of permanganate colour.	2. Active unsaturated group or strong reducing group is present
3. Baeyer's Test: Dissolve little amount of the sample in water or acetone and then add few drops of 1%$KMnO_4$ solution.	3. Reddish colour of Br_2 solution is discharged	3. Ethylenic unsaturation is present
4. Bromine-water: Dissolve little amount of the sample in CCl_4 and add few drops of Br_2-water	4. Gas comes out with smell of NH_3	4. Amido or Imido group present
5. Sodalime Test: Heat little amount of the sample with sodalime		

4.5 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 morter and titurate 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% $FeCl_3$ soluion and acidify with 6(N) H_2SO_4	2. Blue or green colour or ppt.	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 ppt. (ii) Curdy light yellow ppt. (iii) Deep yellow ppt.	1. (i) Cl – present (ii) Br – present (iii) I - present

If Br or I present perform the following test

Experiment	Observation	Inference
1. 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	1. (i) Reddish colour in organic solvent layer (ii) Reddish colour change to violet	1. (i) Bromine Confirmed (ii) Iodine Confirmed

4.6 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 colur persists and then add 1-2 drops of freshly prepared starch solution.	iv) Blue coluration	iv) –COOH gr confirmed

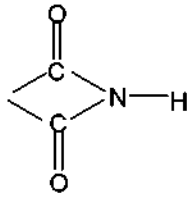
Experiment	Observation	Inference
2. Test for Phenolic-OH group:	2.	2.
i) To 1 ml of the alcoholic of the sample, 2 drops of 1% $FeCl_3$ solution are added	i) Red, blue, green or violet coluration	i) Phenolic –OH gr. present
ii) **Back Dye Test:** In first test tube take about 1 ml of aniline then add few drops of c.HCl. In second test tube prepare about 10% $NaNO_2$ solution. In third test tube dissolve little amount of the sample in 2 ml of 10% NaOH solution. Cool these three tubes in an ice bath. When the solutions are throughly chilled, transfer $NaNO_2$ solution (2) in the acidified aniline solution (1). Now transfer a drop of this diazotised mixture into the alkaline sample solution (3).	ii) Red or Rose red dye	ii) Phenolic -OH gr. Confirm

Experiment	Observation	Inference
3. Test for Carbonyl gr.:	3.	3.
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].	i) Red or Orange red ppt.	i) Carbonylgroup 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 ppt. 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 etanolic 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:	4.	4.
i) A small quantity of the sample is hydrolysed by a strong solution of NaOH. Cool. Acidify with dil. HCl	i) White ppt.	i) Ester gr. present

Experiment	Observation	Inference
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.	ii) A wine red colouration	ii) Ester gr. Confirm

Experiment	Observation	Inference
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 throughly chilled, tranfer $NaNO_2$ solution (b) into acidified sample solution (a). Now pour a drop of this diazotised mixture	6. i) A red dye will form	6. i) Aromatic primary $-NH_2$ present

Experiment	Observation	Inference
to alkaline sodium - 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.	ii) Smell of iso-cyanide comes out	ii)Presence of $-NH_2$ confirm
7. Test for Amido Group:	7.	7.
i) Place little amount of the sample in a test tube and add 2 ml of 10% NaOH solution. Boil the mixture gently.	i) Gas comes out with smell of NH_3 ii) Produces white dense fume incontact of c. HCl moist glass rod. iii) Turns red litmus paper into blue.	i) $-CONH_2$ present
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 HNO_2 (obtained by the reaction between $NaNO_2$ and HCl).	iv) Turns Nesseler's Reagent moist paper into black ii) N_2 gas evolves.	ii) $-CONH_2$ present
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	iii) Bluish red colouration	iii) – $CONH_2$ present

Experiment	Observation	Inference
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.		
8. Test for Imido Group: i) Place little amount of the smple 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 – naphthol in 5 ml 10% NaOH. Place the three mixtures in an ice bath. When the solutions are throughly chilled, tranfer $NaNO_2$ solution into reduced sample solution. Now pour a drop of this diazotised	9. i) Red or orange red dye	9. i) $-NO_2$ gr. Present

Experiment	Observation	Inference
mixture to alkaline sodium - naphthoxide solution.		
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 added to the 5 ml of filtrate and wormed.	ii) Greyish black ppt.	ii) Ar-NO_2 group present.
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.

4.7 Confirmatory test

Experiment	Observation	Inference

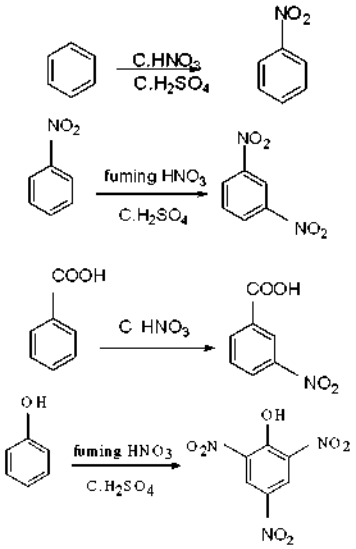
** Write again the confirmatory tests for the functional groups which was found positive during the Detection of Functional Groups

4.8 Preparation of corresponding derivative

4.8.1 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 temparature should not rise above 10^0C. After complete addition, warm the mixture at about 70^0C placing over steam bath for 15-20 minutes. Cool the reaction product and pour it into 25 ml ice- cold water. Seperate the precipitate of nitro compound by filtration and recrystallised from alcohol. Dry and detrmine 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.



4.8.2 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 recrystalise the product from alcohol. Determine the m.p.

4.8.3 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 titurate it with a pastle inside of a fume cupboard until it is converted to a liquid. Add about 10 ml of liquor NH_3, little at a time. When vigorous reaction has ceased, stir, cool and pour into little amount of ice-cool water and filter. Dry and detrmine the m.p.

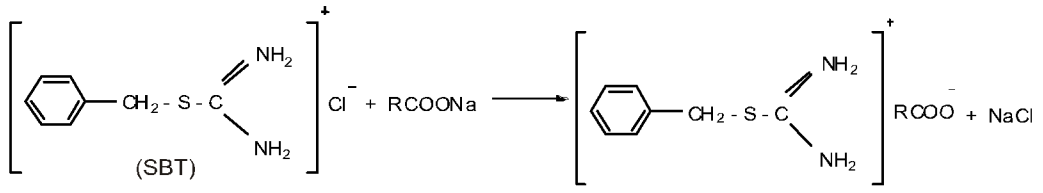
4.8.4 Preparation of Anilide Derivative: [for –COOH gr.]

Place 0.5 g of the sample in a dry mortar with 2 g of PCl_5 and titurate it with a pastle 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, crystallise from alcohol, dry and determine the melting point of the anilide derivative.

4.8.5 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, crystallise from dilute alcohol or hot water.



4.8.6 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 NH_3 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 crystellise from aqueous etanol. Determine the m.p. of the derivative.

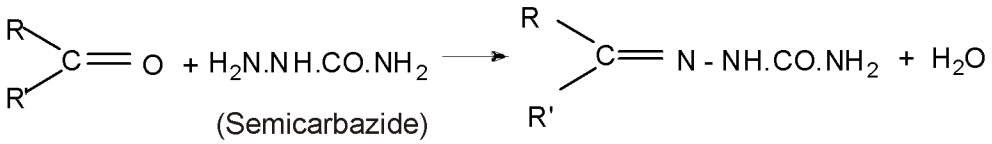
4.8.7 Preparation of 2,4-dinitro phenylhydrazone Derivative: [for =C=O gr.]

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 seperates. 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]

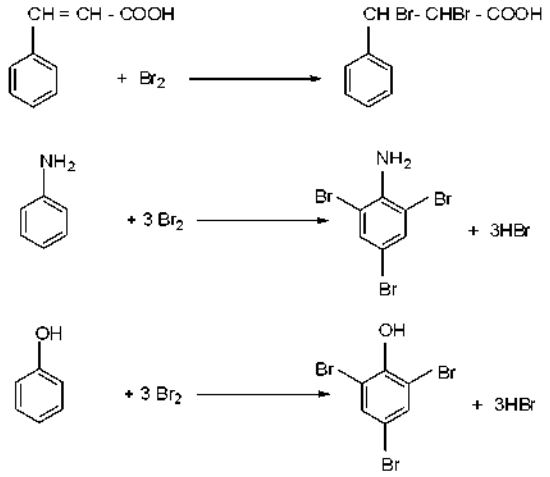
4.8.8 Preparation of Semicarbazide Derivative: [for =C=O gr.]

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 seperates. Filte, dry and recrystallise from alcohol or acetic acid. Determine the melting point of the dried derivative.



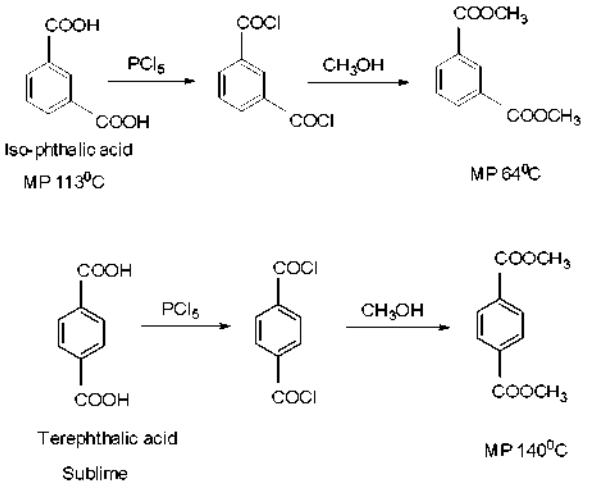
4.8.9 Preparation of Bromo Derivative: [for Ph-OH, Ph-NH_2, Ph-C=C-COOH]

Dissolve 0.5 g of the sample in about 2 ml of glacial acetic acid in a dry test tube. Now add dorp bu 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 colur 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 seperate out. Filter, wash with cold water, recrystallised from alcohol and determine the m.p. of the derivative.



4.8.10 Preparation of Methyl Ester Derivative:

Place 0.5 g of the sample in a dry mortar with 2 g of PCl_5 and titurate it with a pastle 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, wasg the solid with little cold water. Crystallise from aqueous methanol and determine the m.p. of the derivative.

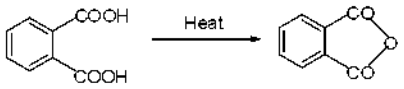


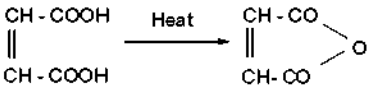
8.8.11 Preparation of Anhydrides of Carboxylic acids: [for dibasic acid]

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 stemed inverted funnel, pluged with cotton, to cover the

material. Heat the basin rapidly, cool , and collect the sublimed product from the funnel and detrmine the m.p. of the product.



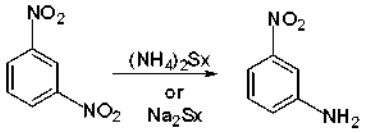


4.8.12 Preparation of Derivatives by Reduction

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

4.8.12.1 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 fitrate with excess NH_4OH solution to precipitate amino- compound. Filter, recrystallise from boiling water and determine the m.p. of the product.

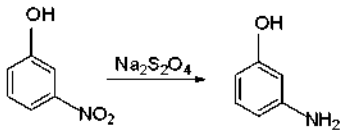


4.8.12.2 Reduction by Sodium Hyposulphide:

(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 mixtuire 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

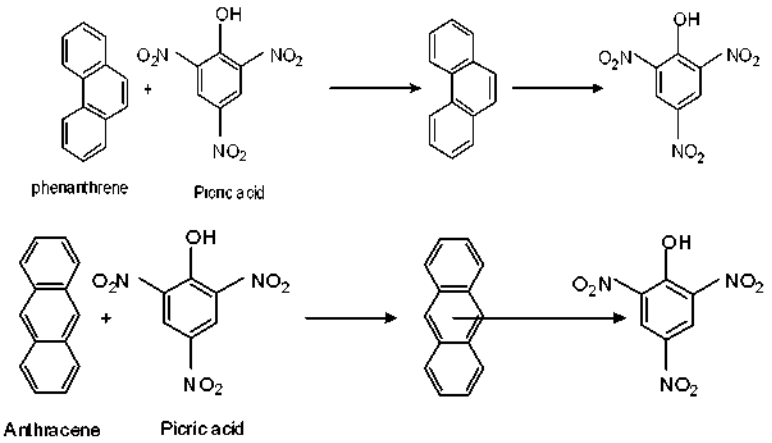
reduction. Filter the mixture at hot condition and cool the filtrate. The solid is then filtered, recrystallised from hot water and determine the m.p. of the product.



4.8.13 Preparation of Picrate Derivative

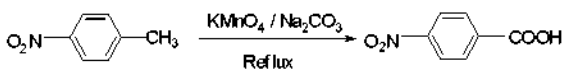
Prepare about 2 ml of saturated solution of picric acid and mix with saturated solution of 0.5 g of sample in benzene and shake the mixture. Allow to stand the mixture for few minutes. Filter, wash the precipitate with few drops of benzene. Dry the precipitate on blotting paper and determine the m.p.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

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



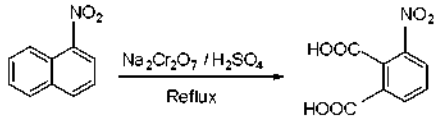
4.8.14 Oxidation by Alkaline $KMnO_4$:

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].



4.8.15 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. Refux the mixture for about 30 minutes. Cool and filter the product under suction. Purify the product after dissolution in aqueous Na_2CO_3 solution and then acdify with H_2SO_4 to precipitate the acid product. Filter, recrystallise from dil. Alcohol and determine the m.p.



4.9 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)

4.10 Chemical reactions involve in organic qualitative analysis

1. 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^-).

$$C,H,O,N,S,X\ (Halogens) \xrightarrow{\text{Fusion with sodium metal}} NaCH, NaSCN, Na_2S, NaX$$

$$Na + CN = NaCN$$

$$Na + C + N + S = NaSCN$$

$$2Na + S = Na_2S$$

$$Na + X(Cl.Br.I) = NaX$$

$$2Na + 2H_2O = 2NaOH + H_2$$

a) Test for Nitrogen:

$$FeSO_4 + 2NaOH = Fe(OH)_2 + Na_2SO_4$$
$$Fe(OH)_2 + 2NaCN = Fe(CN)_2 + 2NaOH$$
$$FeSO_4 + 2NaCN = Fe(CN)_2 + Na_2SO_4$$
$$Fe(CN)_2 + 4NaCN = Na_4[Fe(CN)_6]$$
$$3Na[Fe(CN)_6] + 4FeCl_3 = Fe_4[Fe(CN)_6]_3 + 12NaCl$$

b) Test for Sulphur:

$$Na_2S + (CH_3COO)_2Pb = PbS + 2CH_3COONa$$
$$Na_2S + Na[Fe(CN)_5NO] = Na_4[Fe(CN)_5NOS]$$

c) Test for Nitrogen and Sulphur present together:

$$Fe^{+3} + SCN^- = \underset{\text{Blood red colour}}{[Fe(SCN)]^{+2}}$$

d) Test for Haloges:

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$
$$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O$$

$$NaBr + AgNO_3 \longrightarrow AgBr + NaNO_3$$
$$AgBr + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Br + 2H_2O$$

$$NaI + AgNO_3 \longrightarrow AgI + NaNO_3$$
$$AgI + NH_3 \longrightarrow \text{Insoluble}$$

Reactions of Non-nitrogenous Functional Groups

1. Test for Carboxylic acid group: (–COOH)

a) $NaHCO_3$ Test:

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + CO_2 + H_2O$$

b) Estarification Test:

$$R-\overset{\overset{O}{\|}}{C}-OH + C_2H_6-OH \longrightarrow R-\overset{\overset{O}{\|}}{C}-OC_2H_5 + H_2O$$

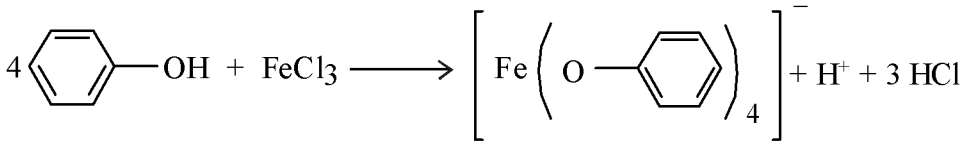
c) Potassium iodate-iodide test:

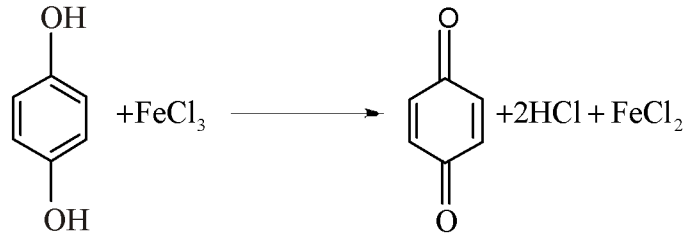
$$6Ph-COOH + 5KI + KIO_3 \longrightarrow 3I_2 + 6Ph-COOK + 2H_2O$$

$$Starch + I_2 \longrightarrow Blue\ colouration$$

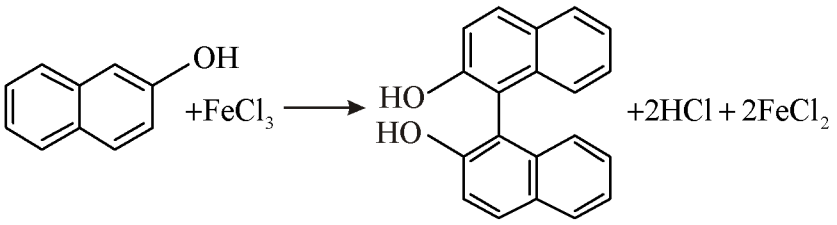
2. Test for Phenolic – OH group:

a) $FeCl_3$ Test:



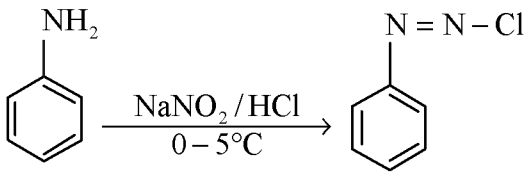


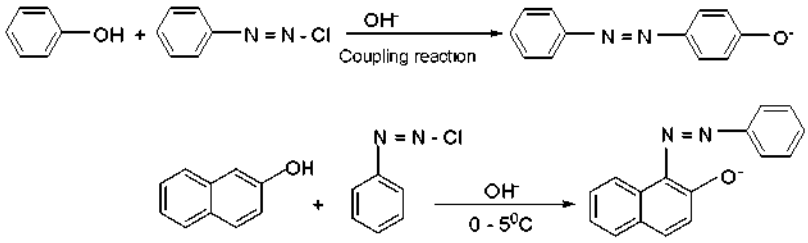
Hydroquinol (Quinol) Benzoquinone



β – Dinaphthol (Green)

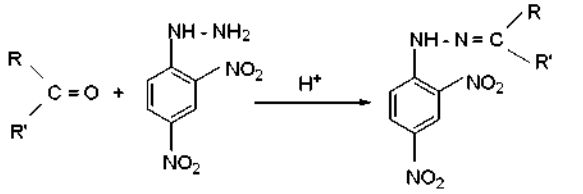
b) Back Dye Test:





3. Test for Carbonyl group:

a) 2,4 – Dinitrophenyl hydrazine Test:

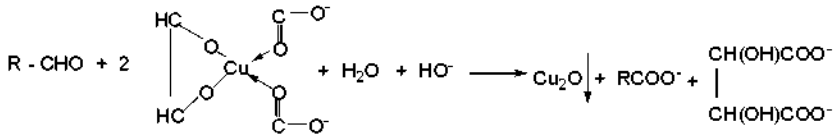


2,4- Dinitrophenyl hydrazone

b) Test for Aldehyde group:

i)Fehling's solution Test:

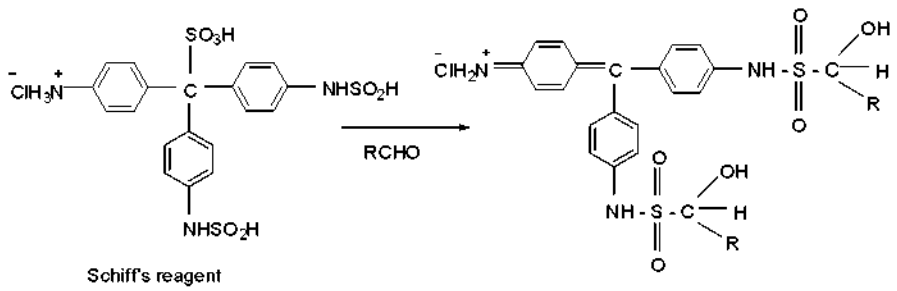
$RCHO + 2\ CuO = Cu_2O + RCOOH$



ii) Tollen's Reagent Test:

$R - CHO + 2\ [Ag(NH_3)_2]OH = 2\ Ag + RCOONH_4 + H_2O + 3\ NH_3$

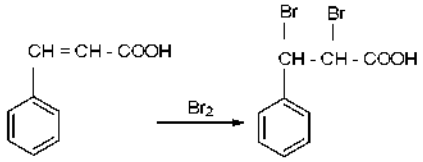
iii) Schiff's Reagent Test:



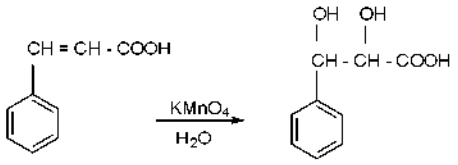
Schiff's reagent

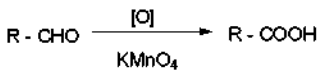
4. Test for Active Unsaturation or Strong Reducing group :

i) Br_2 – water Test;



ii) Baeyer's Test;

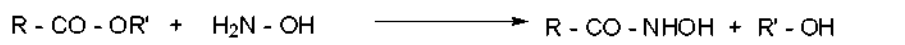


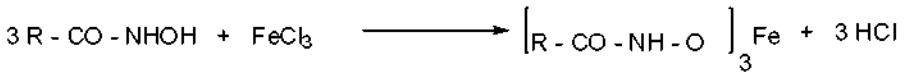


5. Test for Ester group:

i) Hydrolysis test:

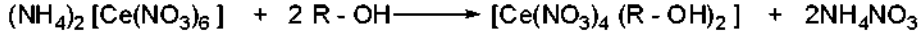
ii) Feigl Test (Hydroxamine test):





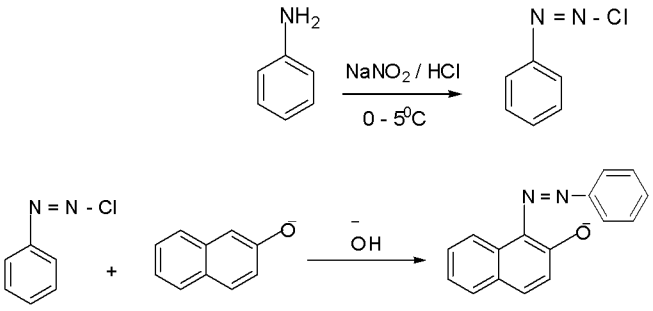
6. Test for Alcoholic –OH group:

(Ceric ammonium nitrate test):

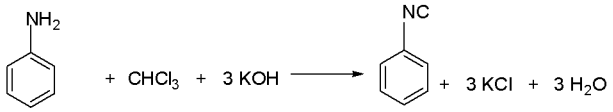


7. Test for Primary Amine:

i) Dye test:

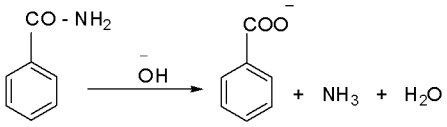


ii) Carbylamine Test:



8. Test for Amido group:

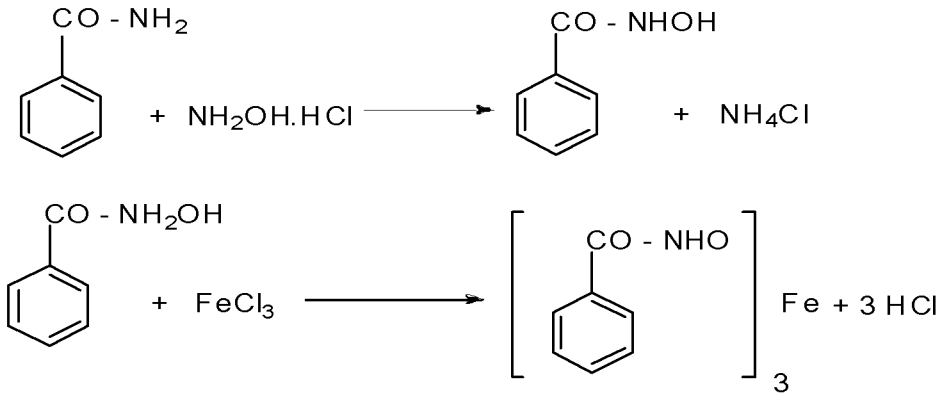
i) Hydrolysis test:



ii) Nitrous acid test:

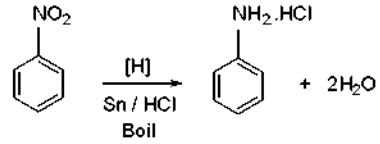
$$C_6H_5 - CO - NH_2 + HO - N = O \longrightarrow C_6H_5 - COOH + N_2 \uparrow + H_2O$$

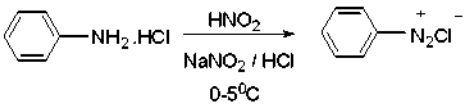
iii) Hydroxylamine hydrochloride test:

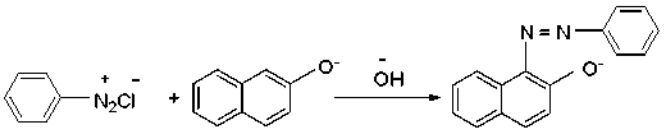


9. Test for Nitro group:

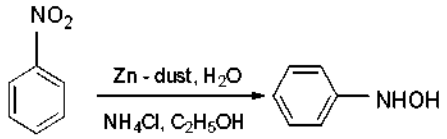
i) Reduction test:

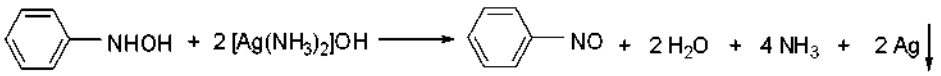






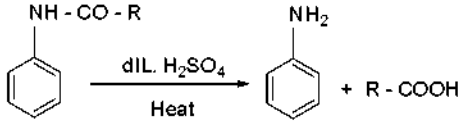
ii) Mulliken - Barker test:





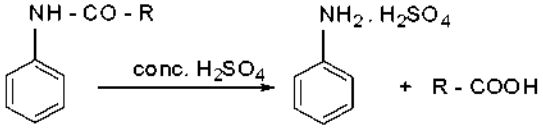
10. Test for Anilido group:

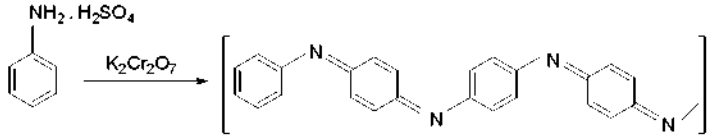
i) Dye test after hydrolysis:



[Same as dye test of aniline]

ii) Tafel's test:

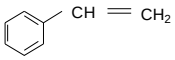
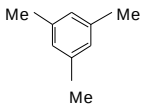




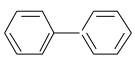
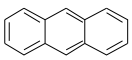
4.11 List of some important organic compounds

Hydrocarbon and halogen compounds:

Liquid

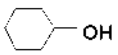
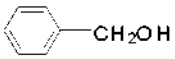
B.P (°C)	Name of the Compound	Properties and derivatives
80	Cyclohexane 	On addition to the fuming HNO_3 yields adipic acid, M.P. 149^0C
142	o-Xylene 	On oxidation with alkaline $KmnO_4$ yields phthalic acid, M.P. 195^0C
146	Styrene 	On oxidation with alkaline $KmnO_4$ yields benzoic acid, M.P. 121^0C
164	Mesitylene 	On oxidation yields trimesic acid , M.P. 300^0C ; methyl ester M.P. 143^0C , ethyl ester M.P. 133^0C

Solid

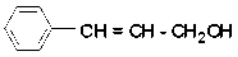
M.P (°C)	Name of the Compound	Properties and derivatives
70	Diphenyl 	On oxidation by chromic acid in glacial acetic acid yields benzoic acid, M.P. 121^0C
216	Anthracene 	Oxidised to anthraquinine M.P. 272^0C ; Picrate M.P. 138^0C
80	Naphthalene 	Oxidised to phthalic acid M.P. 195^0C ; Picrate M.P. 149^0C

Alcohol

Liquid

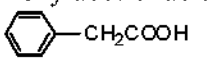
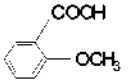
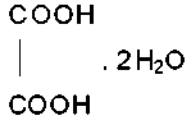
B.P (°C)	Name of the Compound	Properties and derivatives
160	Cyclohexanol (Hexalin) 	On addition to the fuming HNO_3 yields adipic acid, M.P. 149°C
205	Benzol alcohol 	Oxidation with acidic or alkaline $KMnO_4$ yields bezoic acid M.P. 121°C

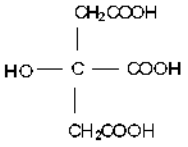
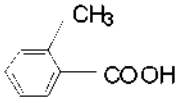
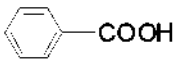
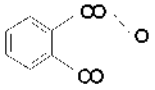
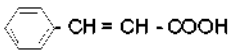
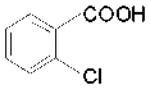
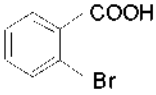
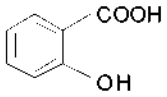
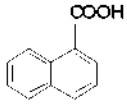
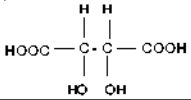
Solid

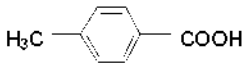
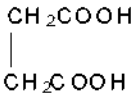
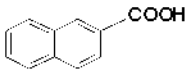
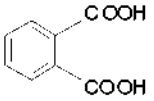
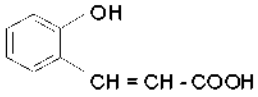
M.P (°C)	Name of the Compound	Properties and derivatives
33	Cinnamyl alcohol 	Oxidised to cinnamic acid M.P. 133°C
166	D-manitol	Hexabenzoate M.P. 124°C ; on heating with PCl_5 yields hexachlorohexane M.P. 137°C

Carboxylic acid

Solid

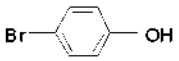
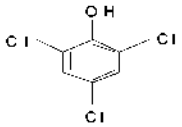
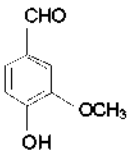
M.P (°C)	Name of the Compound	Properties and derivatives
76	Phenylacetic acid 	SBT M.P. 165°C; Amide M.P. 154°C ; Anilide M.P. 118°COxidation with alkaline $KMnO_4$/NaOH yields benzoic acid M.P. 121°C
100	o-Methoxybenzoic acid 	Amide M.P. 128°C ; Anilide M.P. 131°C
101	Oxalic acid 	SBT M.P 195 (d) ; Dianilide M.P. 246°C

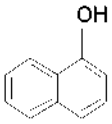
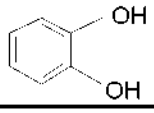
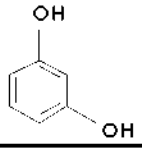
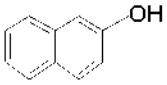
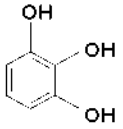
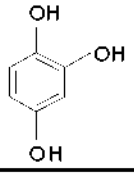
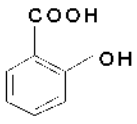
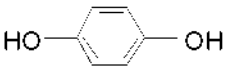
100	Citric acid 	Tri - amide M.P 210°C ; Tri- anilide M.P 192°C ; Methyl ester M.P. 79°C
104	o=Toluic acid 	SBT M.P. 145°C ; Amide M.P. 142°C ; Anilide M.P. 125°C Oxidation with alkaline $KMnO_4$ yields Phthalic acid M.P. 195°C
121	Benzoic acid 	SBT M.P. 167°C ; Amide M.P. 128°C ; Anilide M.P. 164°C
131	Phthalic anhydride 	Reflux with acetic acid and urea yields Phthalimide M.P. 238°C
133	Cinnamic acid 	SBT M.P. 175°C ; Anilide M.P. 153°C
137	o-Chlorobenzoic acid 	Amide M.P. 139°C ; Anilide M.P. 114°C
150	o-Bromobenzoic acid 	SBT M.P. 171°C ; Amide M.P. 155°C ; Anilide M.P. 141°C
155	Salicylic acid 	SBT M.P. 146°C ; Amide M.P. 139°C ; Anilide M.P. 134°C
162	α-Naphthoic acid 	SBT M.P. 135°C ; Amide M.P. 205°C ; Anilide M.P. 205°C
170	(+) Tartaric acid 	Diamide M.P. 195°C (d) ; Dianilide M.P. 264°C

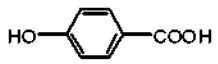
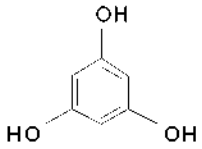
180	p-Tuluic acid 	SBT M.P. 185°c ; Amide M.P. 162°C ; Anilide M.P. 168°C
185	Succinic acid 	SBT M.P. 154°C ; Diamide M.P. 260°C ; Dianilide M.P. 228°C
185	β-Naphthoic acid 	Amide M.P. 192°C ; Anilide M.P. 170°C
195	Phthalic acid 	SBT M.P 157°C ; Ahydride M.P. 131°C ; Diamide M.P. 220°C ; Phthalimide M.P. 231°C
207	o-Coumaric acid 	Amide M.P. 209°C (d) ; Acetyl M.P. 149°C

Phenol

Solid

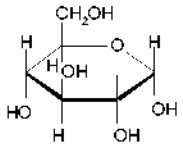
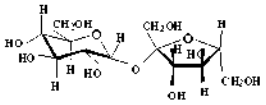
M.P (°C)	**Name of the Compound**	**Properties and derivatives**
63	p-Bromophenol 	Benzoyl M.P. 102°C ; With Br_2-water yields tribromophenol M.P. 95°C
67	s-Trichlorophenol 	Benzoyl derivative M.P. 70°C
80	Vanillin 	Oxime M.P. 117°C Benzoate M.P. 178°C DNP M.P. 270°C

94	α-Naphthol 	Benzoate M.P. 56°C Picrate M.P. 189°C
104	Catechol 	Dibenzoate M.P. 84°C
110	Resorcinol 	Dibenzoate M.P. 117°C
122	β-Naphthol 	Benzoate M.P. 107°C ; Picrate M.P. 156°C
133	Pyrogallol 	Tribenzoate M.P. 89°C Triacetate M.P. 165°C
140	Hydrozyhydroquinone 	Tribenzoate M.P. 120°C Triacetate M.P. 96°C
155	Salicylic acid 	SBT M.P. 146°C Amide M.P. 139°C Anilide M.P. 134°C Acetyl M.P. 135°C
169	Hydeoquinol (Quinol) 	Benzoate M.P. 205°C On mild oxidation yields Benzoquinone (Yellow) M.P. 116°C and/or Quinohydrone (Green) M.P. 171°C

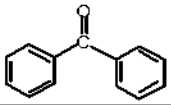
M.P (°C)	Name of the Compound	Properties and derivatives
213	p-Hydoxybenzoic acid 	Red colour in $FeCl_3$ test. SBT M.P. 143°C Anilide M.P. 197°C
218	Phloroglucinol 	Benzoate M.P. 185°C Diacetate M.P. 104°C

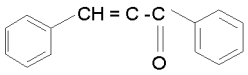
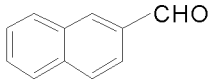
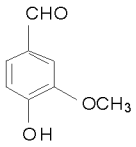
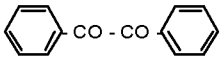
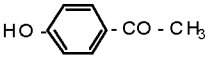
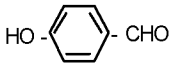
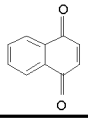
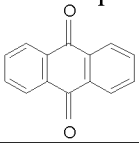
Carbohydrate

Solid

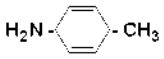
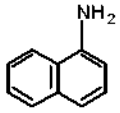
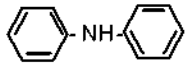
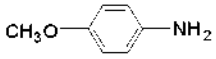
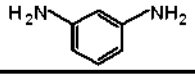
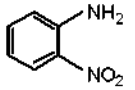
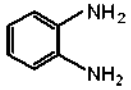
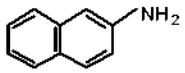
M.P (°C)	Name of the Compound	Properties and derivatives
146	D-Glucose 	To the small quantity of the aqueous sample solution, add a few drops of $(CH_3COO)_2Pb$ solution, heat and add 2 ml of dil. NH_4OH solution. Heat again, a rose pink colouration. On oxidation by HNO_3 yields saccharic acid M.P. 125°C Oxime M.P 137°C Phenylosazone M.P. 205°C
169	Sucrose 	No reaction with Fehling's and Tollen's reagents. On oxidation by HNO_3 yields saccharic acid M.P. 125°C

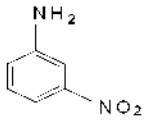
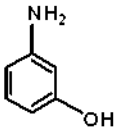
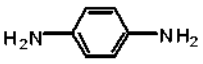
Aldehyde, Ketone and Quinine

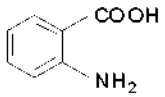
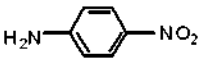
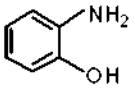
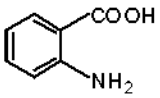
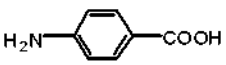
M.P (°C)	Name of the Compound	Properties and derivatives
48	Benzophenone 	Phenylhydrazone M.P. 137°C Semicarbazone M.P. 164°C 2,4 – Dinitrophenylhydrazone M.P. 229°C

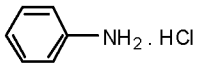
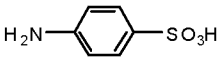
58	Chalcone 	Phenylhydrazone M.P. 118^{0}C Semicarbazone M.P. 168^{0}C 2,4 – Dinitrophenylhydrazone M.P. 244^{0}C
60	β-Naphthaldehyde 	On mild oxidation yields β- Naphthoic acid M.P. 121^{0}C Semicarbazone M.P. 245^{0}C 2,4 – Dinitrophenylhydrazone M.P. 245^{0}C
80	Vanillin 	Oxime M.P. 117^{0}C Benzoate 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-Benezoquinone 	2,4 – Dinitrophenylhydrazone M.P. 186^{0}C
117	p-Hydroxybenzaldehyde 	Phenylhydrazone M.P. 178^{0}CSemicarbazone M.P. 223^{0}C 2,4 – Dinitrophenylhydrazone M.P. 280 ^{0}C
M.P (^{o}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

Amines (Amine, Aminophenol, Aminoacid, Nitroamine)

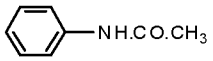
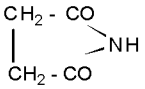
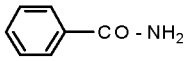
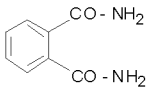
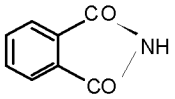
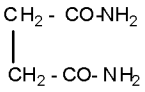
M.P (°C)	**Name of the Compound**	**Properties and derivatives**
45	p-Toluidine 	Benzoyl M.P. 158°C Picrate M.P. 169°C
50	α-Naphthylamine 	Benzoyl M.P. 161°C Picrate M.P. 161°C
53	Diphenylamine 	Benzoyl M.P. 180°C Picrate M.P. 182°C
57	p-Anisidine 	Benzoyl M.P. 154°C Picrate M.P. 117°C
63	m-Phenylenediamine 	Brown ppt. with $NaNO_2$/HCl Dibenzoyl M.P. 240°C
71	o-Nitroaniline 	Benzoyl M.P. 94°C
102	o-Phenylenediamine 	Dibenzoyl M.P. 301°C
111	β-Naphthylamine 	Benzoyl M.P. 162°C Picrate M.P. 195°C

114	m-Nitroaniline 	Benzoyl M.P. 155°C
122	m-Aminophenol 	Monobenzoyl M.P. 174°C Dibenzoyl M.P. 153°C
140	p-Phenylenediamine 	Boiling with dil. $FeCl_3$ or H_2SO_4/MnO_2 yields Benzoquinone M.P. 115°C Picrate M.P. 202°C

M.P (°C)	**Name of the Compound**	**Properties and derivatives**
147	Anthranilic acid 	Benzoyl M.P. 182°C Amide M.P. 108°C Anilide M.P. 126°C
147	p-Nitroaniline 	Benzoyl M.P. 199°C
174	o-Aminophenol 	Dark brown ppt. with $FeCl_3$ Dibenzoyl M.P. 184°C
174	m-Aminobenzoic acid 	Amide M.P. 75°C Anilide M.P. 129°C Acetyl M.P. 250°C
186	p-Aminobenzoic acid 	Benzoyl M.P. 278°C Amide M.P. 183°C

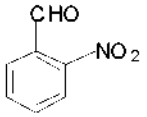
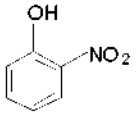
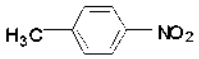
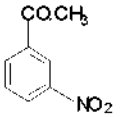
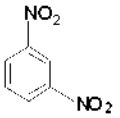
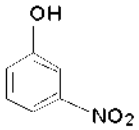
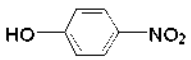
198	Aniline hydrochloride 	Benzoyl M..P. 163^{0}C Picrate M.P.. 165^{0}C
~300	Sulphanilic acid 	With Br_2 – water yields 2,4,6 – Tribromoaniline M.P. 119^{0}C

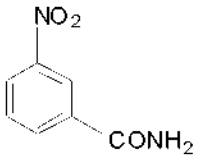
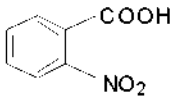
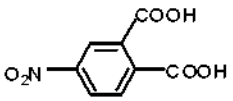
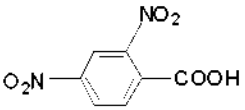
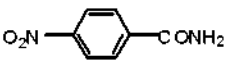
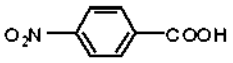
Anilides, Amides and Imides

M.P (^{o}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	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

Nitro Compunds

Nitro – Acids, Phenols, Halides, Aldehydes and Ketones.

M.P (°C)	Name of the Compound	Properties and derivatives
44	o-Nitrobenzaldehyde 	On oxidation with $KMnO_4$ yields o-Nitrobenzoic acid M.P. 144°C Phenylhydrazone M.P. 156°C Semicarbazone M.P. 256°C 2,4- Dinitrophenylhydrazone M.P. 192°C
45	o-Nitrophenol 	Benzoate M.P. 142°C Reduction by boiling with Zn-dust and $CaCl_2$ solution yields o-Aminophenol M.P. 174°C
52	p-nitrotoluene 	Oxidation by $KMnO_4$ or $K_2Cr_2O_7$ yields p-Nitrobenzoic acid M.P. 241°C
80	m-Nitroacetophenone 	Semicarbazone M.P. 261°C 2,4- Dinitrophenylhydrazone M.P. 233°C
90	m-Dinitrobenzene 	Boling with alkaline $K_3Fe(CN)_6$ yields 2,4-Dinitrophenol M.P. 114°C Reduction with NH_4SH yields m-Nitroaniline M.P. 114°C
97	m-Nitrophenol 	Reduction with Zn-dust and $CaCl_2$ solution yields m-Aminophenol M.P. 122°C Benzoate M.P. 95°C
114	p-Nitrophenol 	Benzoate M.P. 142°C

143	m-Nitrobenzamide 	On hydrolysis with dilute NaOH yields m-Nitrobenzoic acid M.P. 140°C
146	o-Nitrobenzoic acid 	Reduction with Sn/HCl yields Anthranilic acid M.P. 144°C Amide M.P. 176°C Anilide M.P 155°C
165	4-Nitrophthalic acid 	Anilide M.P. 192°C Amide M.P. 200°C (d)
183	2,4-Dinitrobenzoic acid 	Amide M.P. 203°C
201	p-Nitrobenzamide 	On hydrolysis with dilute NaOH yields p-Nitrobenzoic acid M.P. 241°C
241	p-Nitrobenzoic acid 	Amide M.P 201°C Anilide M.P. 211°C Methyl ester M.P. 96°C

4.12 Summary

We have learned about the qualitative analysis of signal organic compounds. Physical characteristics are important for determining the compound nature. Lassaigne's Tests is used to detect the special elements present in the compound. After Lassaigne's Test corresponding functional groups are tested according to the procedures discussed. Derivative preparation of the detected functional group are performed and its M.P. confirms the organic compound from literature.

4.13 Questions

Q-1: For what purpose Leissanigene's test is used?

Ans: To dedect the presence of nitrogen, sulphur and halogens in organic compound.

Q-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.

Q-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.

$$2\ Na + 2\ H_2O = 2\ NaOH + H_2$$

Q-4: What is Baeyer's reagent?

Ans: 1% alkaline $KMnO_4$ solution is known as Baeyer's reagent.

Q-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.

Q-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.

Q-7: What is Fehling's solution?

Ans: Fehling's solution is the mixture of two solutions.

a) Fehling – A : 7% $CuSO_4$ solution

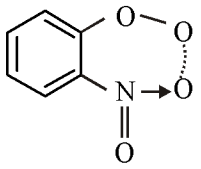
b) Fehling – B : Rochelle salt (sodium potassium tartarate) in 10% NaOH solution

Q-8: What reaction happen when Fehling's solution is treated with aldehyde?

Ans: $R\text{-}CHO + 2\ Cu(OH)_2 = R\text{-}COOH + Cu_2O \downarrow + 2\ H_2O$

Q-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.



Q-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.

$$Fe_4[Fe(CN)_6]_3 + 12NaOH \longrightarrow 4Fe(OH)_3 + 3Na_4[Fe(CN)_6]$$

Blue Brown Colourless

Q-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;

$$3\ NaCNS + FeCl_3 \longrightarrow 3\ NaCl + Fe(CNS)_3$$

$$Fe(CNS)_3 + 3\ NaCNS \longrightarrow Na_3[Fe(CNS)_6]$$

$$Na_3[Fe(CNS)_6] + FeCl_3 \longrightarrow 3\ NaCl + Fe[Fe(CNS)_6]$$

(Red)

Q-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.

Q-13: Why dose benzoin response to Tollen's test?

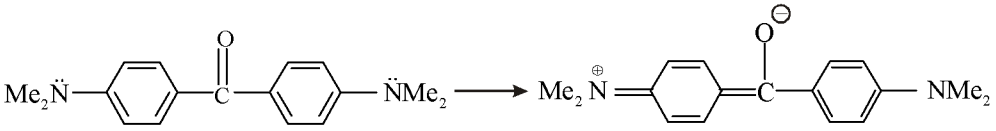
Ans: The - CO. CHOH – group present in benzoin shows reducing properties like – CHO group.

Q-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.

Q-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.



Q-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}.

Q-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 ppt. of FeS.

$$Na_2S + FeSO_4 = FeS + Na_2SO_4$$

Q-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.

Q-19: What test do you suggest for nitroanilides and nitroanilines?

Ans: Mulliken and Barker's test.

Unit-5 □ Quantitative Analysis of Organic Compounds

Structure

5.1 Objectives

After studying and performing this experiment, learner should be able to

- Determine the amount of glycine in the given sample,
- Describe formylation reaction, and perform acid-base titration using standard alkali
- Determine the amount of glucose in the given sample,
- Describe oxidation reactions of sugars with Fehling's solutions, and perform redox titrations using standard solution of Fehling's Solutions.
- Know about iodimetric estimation of ascorbic acid
- To estimate amount of aniline and phenol present in solution by bromination method

- Describe the oxidation reaction of formaldehyde with sodium hypoiodite solution, and perform iodometric titration to determine the amount of formaldehyde as in given formaldehyde solution
- Estmation of Acetic Acid in Commercial Vinegar
- Perform the estimation of Urea by Hypobromite Method
- Determine Saponification Value of Oil/ Fat/ Ester through estimation

5.2 Introduction

In the previous unit we have learned about the qualitative analysis of organic compounds. Here we will learn about the quantitative analysis of organic compounds. The amount of organic substances present in a solution can be determined using titrimetric analysis like metal ions. To carry out the titrimetric analysis, we use some basic organic reactions which will be discussed in the principles of the experiment. In this unit we will discuss ten such experiments including the estimation of sugar, vitamin, aldehyde, organic acid etc.

5.3 Estimation of glycine by Sorensen's formal method

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 direcly with alkali.

$$H_2N-CHR-COOH \overset{H_2O}{\rightleftharpoons} H_3\overset{\oplus}{N}-CHR-COO^{\ominus}$$

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

$$H_2C=N-CH_2-COOH + NaOH \longrightarrow H_2C=N-CH_2-COONa + N_2O$$

1000 ml (N) NaOH solution ≡ 1 g equivalent of glycine ≡ 75 g of glycine

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) Formaline 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].

Procedure:

1. Standardisation of NaOH solution:
   Standardise the NaOH solution with the standard oxalic acid solution using phenolphthalein indicator.
2. Preparation of glycine solution:
   Make up the volume of given unknown solution of glycine to 100 ml in a volumetric flask.
3. Estimation of glycine:
   Take 10 ml ,of formaline solution in a 250 ml conical flask, add 25 ml of distilled water and 1-2 drops of phenolphthalein indicator. Neutralise 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. Ignor 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.

Experimental Results:

Table-1: Preparation of 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.

Initial weight (g)	Final weight (g)	Weight taken (g)
W_1	W_2	$W = W_1 - W_2$

∴ Strength of Oxalic acid = w/ 1.5758 (N/10) = S (N)

Table-2: Standardisation of NaOH solution

No. of obs.	Volm. of oxalic acid (ml)	Burette reading		Volm. of NaOH (ml)	Mean volm. of NaOH (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_1
3.	25	...	...	...	

Strength of NaOH solution :

$25ml \times S(N) = V_1 ml \times S_1 \qquad \therefore S_1 = 25 \times S/V_1(N)$

Table-3: Estimation of Glycine

No. of obs.	Volm. of glycine (ml)	Burette reading		Volm. of NaOH (ml)	Mean volm. of NaOH (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_2
3.	25	...	...	...	

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

$V_2 \times S_1$ ml (N) NaOH solution ≡ $0.075 \times V_2 \times S_1$ g of glycine / 25 ml

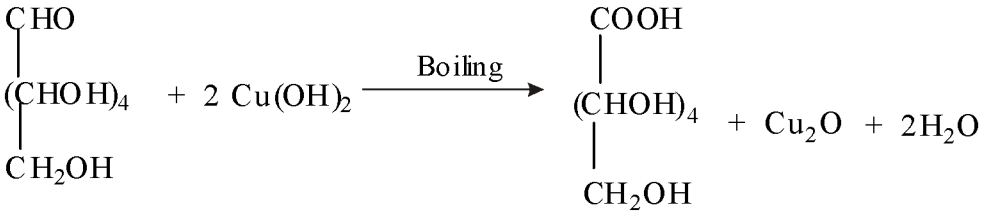
≡ $0.075 \times V_2 \times S_1 \times 40$ g of glycine / 1000 ml

∴ Amount of glycine in supplied solution = $0.075 \times V_2 \times S_1 \times 40$ g / lit.

5.4 Estimation of glucose by titration using Fehling's solution

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.

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]

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. 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.

5. 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 supplide 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.]

Experimental results:

Table – 1: 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.

Initial weight (g)	Final weight (g)	Weight taken (g)
W_1	W_2	$W = W_1 - W_2$

Table – 2: Standardisation of Fehling's Solution

No. of obs.	Volm. of Fehling's solution (ml)	Burette reading		Volm. of Glucose solution (ml)	Mean volm. 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.	Volm. of Fehling's solution (ml)	Burette reading		Volm. of supplied Glucose solution (ml)	Mean volm. of supplied glucose solution (ml)
		Initial	Final		
1.	20	0	...	...	
2.	20	...	...	...	V_1
3.	20	...	...	...	

Calculation:

20 ml Fehling's solution ≡ V ml of standard glucose solution

20 ml Fehling's solution ≡ V ml of supplied glucose solution

250 ml standard glucose solution ≡ Wg of glucose

V ml of standard glucose solution ≡ W × V/250g of glucose

∴ V_1 ml of the supplied glucose solution ≡ V ml of standard solution

≡ W × V/250g of glucose

∴ 1000 ml of supplied glucose solution ≡ (W × V/ V_1) × 4 g of glucose

∴ Amount of glucose present in supplied solution = (W × V/ V_1) × 4g

∴ % of glucose present in supplied solution = (W × V/ V_1) × 0.4g

Note:

1) The entire titration should be completed withn 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.

5.5 Estimation of sucrose by titration using Fehling's solution

Principle:

Sucrose is non-redusing 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.

$$C_{12}H_{22}O_{11} \quad H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$

$\therefore$ 342g of sucrose = 360g of inverted sugar

These inverted sugars are titrated with standard Fehling's solution using methylene blue as indicator.

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

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. Tranfer 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.

Experimental Result:

Table – 1: 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.

Initial weight (g)	Final weight (g)	Weight taken (g)
W_1	W_2	$W = W_1 - W_2$

Table – 2: Standardisation of Fehling's Solution

No. of obs.	Volm. of Fehling's solution (ml)	Burette reading		Volm. of Glucose solution (ml)	Mean volm. of Standard glucose solution (ml)
		Initial	Final		
1.	20	0	...	...	V
2.	20	...	...	...	
3.	20	...	...	...	

Table – 3: Estimation of Supplied Sucrose Solution

No. of obs.	Volm. of Fehling's solution (ml)	Burette reading		Volm. of supplied Sucrose solution (ml)	Mean volm. of supplied Sucrose solution (ml)
		Initial	Final		
1.	20	0	...	...	V_1
2.	20	...	...	...	
3.	20	...	...	...	

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

≡ $(250 \times W \times V)/(V_1 \times 250)$ g of glucose

= $(W \times V)/V_1$ g of glucose

Since, 360 g glucose ≡ 360 g of Inverted sugar ≡ 342 g of sucrose

∴ $(W \times V) / V_1$ g of glucose ≡ $(342 \times W \times V) / (360 \times V_1)$ g of sucrose in 25 ml of the supplied solution

∴ Amount of sucrose present in the supplied solution

= $(342 \times W \times V \times 40) / (360 \times V_1)$ g in 1 lit.

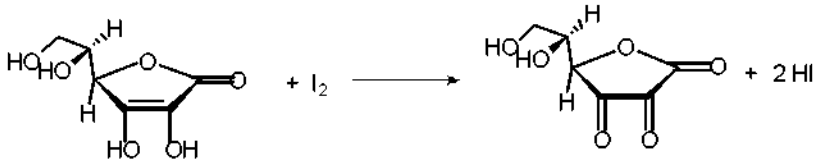
= $(38 \times W \times V) / V_1$ g / lit.

Note:

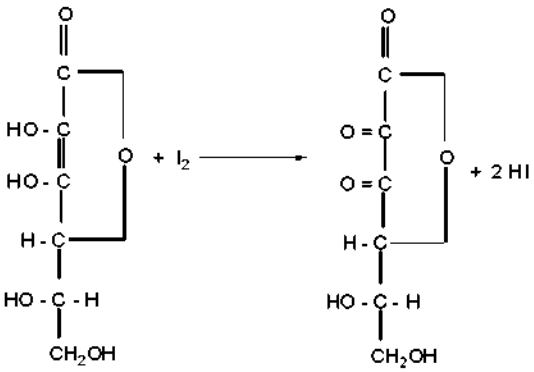
1) **The entire titration should be completed within 3-4 minutes.**
2) **The solution should be shaken before use.**
3) **Titration should be done under boiling condition to prevant the backward aerial oxidation.**

5.6 Estimation of Vitamin – C (reduced)

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



L-Ascorbic acid Dehydro-L- ascorbic acid

According to the molecular formula :

$$C_6H_6O_6 + I_2 \longrightarrow C_6H_6O_6 + 2HI$$

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 thiosulphate gives the amount of iodine consumed and hence the amount of vitamin C.

According to the iodimetry, we have

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

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 $Na_2S_2O_3$ ≡ $\frac{1}{2}$ mole of $C_6H_8O_6$

∴ 1000 ml of (N) $Na_2S_2O_3$ solution ≡ $\frac{176.2}{2}$ g of vitamin C = 88.1 g of vitamin C

∴ 1 ml … … … … ≡ 0.0881 g of vitamin C = 88.1 mg of vitamin C

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].

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 x *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.

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/0.6129 (N/20)= S (N)

Table – 2: Standardisation of thiosulphate solution against standard $K_2Cr_2O_7$ solution:

No. of obs.	Volm. of $K_2Cr_2O_7$ (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ (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.	Volm. of Solution (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_2
3.	25	...	...	...	

Table – 4: Estimation of vitamin C:

No. of obs.	Volm. of vitamin C (ml)	Volm. of I_2 solution (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ (ml)
			Initial	Final		
1.	25	×25	0	...	...	
2.	25	×25	...	...	...	V_3
3.	25	×25	...	...	...	

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 × S/ V_1 (N) = S_1 (N)

25 ml of I_2 – solution ≡ V_2 ml of S_1 (N) thiosulphate solution

∴ (25 ml × x) ml iodine solution ≡ x V_2 ml of S_1 (N) thiosulphate solution

Now, (25 × x) ml I_2 – solution ≡ (25 ml vitamin C solution + V_3 ml of S_1 (N) thiosulphate solution)

∴ 25 ml of vitamin C solution ≡ (x V_2 – V_3) ml of S_1 (N) thiosulphate solution

Since, 1 ml of (N) thiosulphate solution ≡ 88.1 mg of vitamin C

Since, 25 ml of vitamin C solution ≡ (x V_2 – V_3) ml of S_1 (N) thiosulphate solution

∴ ≡ 88.1 (x V_2 – V_3) × S_1 mg of vitamin C

∴ 1 ml of vitamin C solution ≡ 88.1 (x V_2 – V_3) × S_1 / 25 mg of vitamin C

∴ strength of the vitamin C solution = 88.1 (x V_2 – V_3) × S_1 × 1000/ 25 mg/ lit.

= 88.1 (x V_2 – V_3) × S_1 × 40 mg/ lit.

Or, = 88.1 (x V_2 – V_3) × S_1 × 100/ 25 mg %

= 88.1 (x V_2 – V_3) × S_1 × 4 mg %

5.7 Estimation of aniline by bromination (bromate–bromide) method:

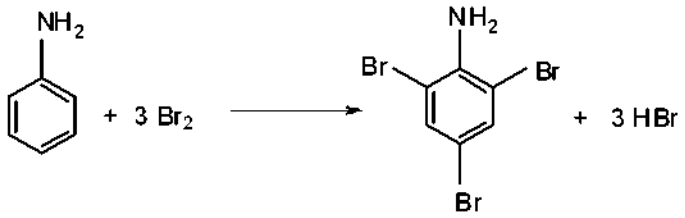
Principle:

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., 1g 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 $C_6H_5NH_2$

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]

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 S 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 upto the 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 supplide aniline spolution 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 intemately. 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.

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	$W_1 = W_1 - W_2$

Table – 2: Standardisation of $Na_2S_2O_3$ solution against standard $KBrO_3$-KBr solution:

No. of obs.	Volm. of $KBrO_3$– KBr (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln, (ml)	Mean volm. of $Na_2S_2O_2$ soln. (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V
3.	25	...	...	...	

Table – 3: Estimation of Aniline

No. of obs.	Volm. of Aniline solution + $KBrO_3$–KBr (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1.	25 + 50	0	...	...	
2.	25 + 50	...	...	...	V_1
3.	25 + 50	...	...	...	

Calculation:

Strength of $KBrO_3$ – KBr solution ≡ W / 0.6958 (N/10)

The reaction in acid medium is

$BrO_3^- + 6\ H^+ + 6\ e = Br^- + 3\ H_2O$

∴ Equivalent weight of $KBrO_3$ = 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

$= 0.62044 \times (2V - V_1) \times Sg$ / lit.

5.8 Estimation of Phenol by bromination (bromate-bromide) method

Principle:

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 –

$$KBrO_3 + 5KBr + 6HCl \longrightarrow 3Br_2 + 6KCl + 3H_2O$$

$$Br_2 + 2\ KI = I_2 + 2\ KBr$$

$$2\ Na_2S_2O_3 + I_2 = 2\ NaI + Na_2S_4O_6$$

$$\therefore KBrO_3 = 3\ Br_2 = C_6H_5OH = 3I_2 = 6\ Na_2S_2O_3$$

$\therefore$ 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

$$BrO_3^- + 6H^+ + 6C \rightleftharpoons Br^- + 3H_2O$$

$\therefore$ Equivalent weight of $KBrO_3$ = M. Wt./6 = 167/6 = 27.8333

Thus, 1000 ml (N) $KBrO_3$ solution contain 27.8333 g of $KBrO_3$

$\therefore$ 250 ml 0.1 (N) ... . 27.8333/40 = 0.6958 g of $KBrO_3$

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]

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. Peparation of phenol solution:

   Diluted the supplied phenol soution 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 supplide aniline spolution 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 intemately. 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.

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.	Volm. of $KBrO_3$– KBr (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V
3.	25	...	...	...	

Table – 3: Estimation of Aniline

No. of obs.	Volm. of Phenol solution + $KBrO_3$– KBr (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1.	25 + 50	0	...	...	
2.	25 + 50	...	...	...	V_1
3.	25 + 50	...	...	...	

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., $25 \times W/0.6958\ (N/10) = V \times S_2$

$\therefore S_2 = (25 \times W)/(0.6958 \times V \times 10)\ (N) = S\ (N)$

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

$\therefore$ 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

$\therefore (2V - V_1)$ ml S (N) $Na_2S_2O_3$ solution ≡ $0.093066 \times (2V - V_1) \times S$ /6 g of Phenol in 25 ml solution

$\therefore$ The amount of Phenol in supplied sample solution ≡ $0.093066 \times (2V - V_1) \times S \times 40$ /6 g in 1000 ml

$= 0.62044 \times (2V - V_1) \times Sg$ /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.***

5.9 Estimation of formaldehyde (formalin)

Principle:

Formaldehyde, HCHO, may be estimated iodometrically. Formaldehyde 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 ($S_4O_6^{-2}$).

$$I_2 + 2NaOH = NaOI + NaI + H_2O$$

$$\underline{HCHO + NaOI + NaOH = HCOONa + NaI + H_2O}$$

$$HCHO + I_2 + 3NaOH = HCOONa + 2NaI + 2H_2O$$

$$NaOI\ (excess) + NaI + 2HCl = 2NaCl + I_2 + H_2O$$

$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

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

$$\therefore HCHO \equiv I_2 \equiv 2S_2O_2^{-2}$$

$$\therefore S_2O_3^{-2} \equiv \tfrac{1}{2}HCHO \equiv 1 \text{ equivalent}$$

$\therefore$ 1000ml of (N) thiosulphate solution $\equiv$ 15g of HCHO

Or, 1 ml of (N) thiosulphate solution $\equiv$ 0.015g of HCHO

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 formalinl with distilled water in a 250 ml volumetric flask upto the mark and supply 9 - 12 ml to each student]

Procedure:

1. Preparation of 250 ml S (N/10) $K_2Cr_2O_7$ solution:

Table – 1:

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)

2. Preparation of 0.1 (N) iodine solution:

   Dissolve 1.27g of I_2 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 soution 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 $K_2Cr_2O_7$ 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 experiment thrice.

6. Estimation of Formaldehyde:

   Take 25 ml of the formalin solution in a 500 ml conical flask follwed 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 atleast 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.

Experimental Results:

Table – 2: Standardisation of $Na_2S_2O_3$ solution against standard $K_2Cr_2O_7$ solution:

No. of obs.	Volm. of $K_2Cr_2O_7$ (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_1
3.	25	...	...	...	

Table – 3: Standardisation of I_2 solution against standard $Na_2S_2O_3$ solution:

No. of obs.	Volm. of I_2-soln. (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_2
3.	25	...	...	...	

Table – 4: Back titration for the estimation of Formalin solution:

No. of obs.	Volm. of Formalin (ml)	Volm. of I_2 solution (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ (ml)
			Initial	Final		
1.	25	50	0	...	...	
2.	25	50	...	...	...	V_3
3.	25	50	...	...	...	

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 + 50 ml 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.

5.10 Estmation of acetic acid in commercial vinegar

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. Acetic acid content in commercial vinegar can be estimated

by alkalimetry. A measured quantity of vinegar is diluted to a definite volume and an alliquot is titrated with a standard NaOH solution using phenolphthalein indicator as it is a titration of a weak acid and strong base.

Chemicals Required:

i) Standard S (N/20) oxalic acid
ii) (N/20) NaOH solution
iii) Vinegar solution (Unknown)
iv) Phenolphthalein indicator

Procedure:

1. Preparation of 250 ml standard S (N/20) oxalic acid solution:

Table – 1:

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	$W-W_1-W_2$	0.7875	250	W/0.7875 (N/20) = S(N)

2. Preparation of S (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.

Experimental Results:

Table – 2: Standardisation of NaOH solution against standard (N/20) oxalic acid solution:

No. of obs.	Volm. of oxalic acid (ml)	Burette reading		Volm. of NaOH soln. (ml)	Mean volm. of NaOH soln. (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_1
3.	25	...	...	...	

Table – 3: Estimation of Acetic Acid agaist standard NaOH solution:

No. of obs.	Volm. of vinegar acid (ml)	Burette reading		Volm. of NaOH soln. (ml)	Mean volm. of NaOH soln. (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_2
3.	25	...	...	...	

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 $\quad \therefore S_1 = 25 \times S / V_1$ (N)

Reaction:

$CH_3COOH + NaOH = CH_3COONa + H_2O$

i.e. 40 g NaOH ≡ 60 g CH_3COOH ≡ 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_2ml 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 ... ... 60 $\times$ S_1 $\times$ V_2 $\times$ 250 / 1000 $\times$ 25 g of acetic acid

$\therefore$ 1000 ml ... ... 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.

5.11 Estimation of urea (hypobromite method)

Principle:

When 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.

$$OBr^- + 2I^- + 2H^+ = I_2 + Br^- + H_2O$$

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

$$\therefore CO(NH_2)_2 \equiv 3OBr^- \equiv 3I_2 \equiv 6S_2O_3^-$$

Or, $S_2O_2^- \equiv 1/6\ CO(NH_2)_2 \equiv 1$equivalent

$\therefore 1000ml(N)\ S_2O_3^-$ solution $\equiv 60/6$ or 10g of urea.

Since hypobromite is very unstable when prepared directly by the reaction between Br_2 and alkali. So it is advantageneous to produce hypobromite in situ by adding excess bromide to the solution of hypochlorite.

$$OCl^- + Br^- = OBr^- + Cl^-$$

Chemicals Required:

i) Standard S (N/20) $K_2Cr_2O_7$ solution

ii) S (N/20) $Na_2S_2O_3$ solution

iii) 10% KI solution

iv) 1% starch solution

v) S (N/20) NaOCl solution

vi) S (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]

Procedure:

1. Preparation of 250 ml of (N/20) $K_2Cr_2O_7$ solution:

Table – 1:

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/20) $=S_1(N)$

2. Preparation of 250 ml of S (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 soution with distilled water in a 250 ml volumetric flask upto the mark.

6. Standardisation of (N/20) $Na_2S_2O_3$ solution against standard (N/20) $K_2Cr_2O_7$ 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 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 against standard (N/20) $Na_2S_2O_3$ 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.

Experimental Result

Table – 2: Standardisation of $Na_2S_2O_3$ solution against standard $K_2Cr_2O_7$ solution:

No. of obs.	Volm. of $K_2Cr_2O_7$ (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_2
3.	25	...	...	...	

Table – 3: Standardisation of Hypobromite solution against standard $Na_2S_2O_3$ solution:

No. of obs.	Volm. of hypobromite soln. (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln. (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_3
3.	25	...	...	...	

Table – 4: Back titration for the estimation of Urea solution:

No. of obs.	Volm. of Urea soln. (ml)	Volm. of hypobromite soln. (ml)	Burette reading		Volm. of $Na_2S_2O_3$ soln. (ml)	Mean volm. of $Na_2S_2O_3$ soln.(ml)
			Initial	Final		
1.	25	50	0	...	...	
2.	25	50	...	...	...	V_4
3.	25	50	...	...	...	

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 $\equiv$ 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 $\equiv$ 10g 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 /25ml

25 ml urea solution contain $0.01 \times (2V_3 - V_4) \times S$ g of urea

$\therefore$ 1000 ml ... ... $0.01 \times (2V_3 - V_4) \times S \times 40$ 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.

5.12 Estimation of saponification value of oil/ fat/ ester

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.

A known weight of Ester/Oil/Fat is completely saponified by boiling with measured excess of standard alcoholic KOH solution. The unreacted alkali is back titrated with a standard acid solution.

$$\begin{array}{l} H_2C-COOR_1 \\ \quad | \\ H_2C-COOR_2 + 3KOH \longrightarrow \\ \quad | \\ H_2C-COOR_3 \end{array} \begin{array}{l} CH_2OH \\ \quad | \\ CH_2OH \\ \quad | \\ CH_2OH \end{array} \quad \begin{array}{l} R_1COOK \\ \\ + \quad R_2COOK \\ \\ R_3COOK \end{array}$$

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

Procedure:

1. Preparation of 100 ml of (N/2) oxalic acid solution:

Table – 1:

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/20) $=S_1(N)$

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. Repeate 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. Repeate 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 S (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 S (N/2) HCl solution using phenolphthalein as indicator till the solution turns from pink to colourless. Record the titrate value (V_5 ml).

7. Blank titration:

   Pipette out 25 ml of the standard S (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 (V_4 ml).

Experimental Result:

Table – 2: Standardisation of KOH solution against standard (N/2) oxalic acid solution:

No. of obs.	Volm. of KOH soln. (ml)	Burette reading		Volm. of oxalic acid soln. (ml)	Mean volm. of oxalic acid soln. (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.	Volm. of KOH soln. (ml)	Burette reading		Volm. of oxalic acid soln. (ml)	Mean volm. of oxalic acid soln. (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_3
3.	25	...	...	...	

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 excess alkali:

No. of obs.	Volm. of KOH soln. (ml)	Burette reading		Volm. of HCl (ml)	Mean volm. of HCl soln. (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_5
3.	25	...	...	...	

Table – 6: Blank titration of KOH solution:

No. of obs.	Volm. of KOH soln. (ml)	Burette reading		Volm. of HCl (ml)	Mean volm. of HCl soln. (ml)
		Initial	Final		
1.	25	0	...	...	
2.	25	...	...	...	V_4
3.	25	...	...	...	

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 x S_2 i.e., V_1 ml × S_1 (N) = 10 ml × S_2

$\therefore S_2 = V_1 \times S_1 / 10$ (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 × S_2 (N) = V_3 ml × S_3

$\therefore S_3 = 10 \times S_2 / V_3$ (N)

3. Blank titre value (25 ml KOH solution) ≡ V_4 ml S_3 (N) HCl solution

W_5 g oil + 25 ml KOH solution ≡ $(V_4 - V_5)$ ml S_3 (N) HCl solution

≡ $(V_4 - V_5) \times S_3$ ml (N) HCl solution

≡ $(V_4 - V_5) \times S_3$ ml (N) KOH solution

We have, 1000 ml (N) KOH solution ≡ 56.1 g of KOH

$\therefore (V_4 - V_5) \times S_3$ ml (N) KOH solution ≡ $0.0561 \times (V_4 - V_5) \times S_3$ g of KOH

Or, W_5 g of oil ≡ $0.0561 \times (V_4 - V_5) \times S_3$ g of KOH

≡ $56.1 \times (V_4 - V_5) \times S_3$ mg of KOH

$\therefore$ 1 g oil ≡ $56.1 \times (V_4 - V_5) \times S_3 / W_5$ mg of KOH

$\therefore$ The saponification value of the given oil = $56.1 \times (V_4 - V_5) \times S_3 / W_5$ mg

5.13 Summary

- 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.
- The Fehling's solution is standardised by tritrating with standard glucose solution using methylene blue as indicator.
- Titration of glucose should be done fast under boiling condition to prevent the backward aerial oxidation
- Sucrose is non-redusing sugar, so it can be estimated by converting it into two reducing sugars by hydrolysis and are titrated with standard Fehling's solution using methylene blue as indicator.
- Aniline and Phenol are estimated by the reaction with measured excess of standard $KBrO_3$- KBr solution in presence of acid.
- During the estimation of Aniline and Phenol the flask always is stopped after the addition of reagents to prevent the loss of bromine due to its high volatility.
- Formaldehyde, HCHO, may be estimated iodometrically using hypoiodite.
- Acetic acid content in commercial vinegar can be estimated by alkalimetry using standard NaOH solution as base and phenolphthalein as indicator similarly as a titration of a weak acid and strong base.
- Urea reacts with alkaline hypobromite solution and it is oxidised to nitrogen.
- 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.

5.14 Questions

Q-1: What is the advantage of dichromatometry?

Ans: $K_2Cr_2O_7$ is a primary standard as such it does not require standardisation.

Q-2: 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.

Q-3: 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.

Q-4: How starch acts as an indicator?

Ans: Starch is a mixture of amylose and amylopectin. (I_3^-) 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.

Q-5: 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.

Q-6: 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).

Q-7: 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.

Q-8: 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.

Q-9: Why saponification value of oil is determined?

Ans: The determination of saponification value indicates the rancidity of the oil as well as its purity.

Q-10: What is saponification reaction?

Ans: Discussed in principle.

Q-11: 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.

Q- 12: 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.

Q- 13: 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.

Q-14: 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.

Q-15: what is ascorbic acid?

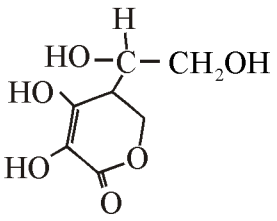
Ans: Ascorbic acid is vitamin C, which is water soluble vitamin.

Q-16: What are the natural sources of ascorbic acid?

Ans: In juice of fresh fruits and vegetables.

Q-17: 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.



Q-18: 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.

Q-19: 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.

$$KBrO_3 + 5\ KBr + 6\ HCl = 3\ Br_2 + 6\ KCl + 3\ H_2O$$

Q-20: 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.

Q-21: 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.

$$KBrO_3 + 5\ KBr + 6\ HCl = 3\ Br_2 + 6\ KCl + 3H_2O$$

Q-22: 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.

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