INORGANIC & PHYSICAL CHEMISTRY

M.Sc. Chemistry

First Year, SEMESTER-II,

PRACTICAL – I : 205CH24

Lesson Writers

Prof. R. Ramesh Raju
Dept. of Chemistry
University College of Sciences
Acharya Nagarjuna University

Prof. K. Rambabu
Dept. of Chemistry
University College of Sciences
Acharya Nagarjuna University

Editor & Academic Advisor
Prof. M. Subba rao
Department of Chemistry
Acharya Nagarjuna University

DIRECTOR, I/c.
Prof. V. Venkateswarlu
M.A., M.P.S., M.S.W., M.Phil., Ph.D.
CENTRE FOR DISTANCE EDUCATION
ACHARYA NAGARJUNA UNIVERSITY
NAGARJUNA NAGAR 522 510
Ph: 0863-2346222, 2346208
0863- 2346259 (Study Material)
Website www.anucde.info
E-mail: anucdedirector@gmail.com

M.Sc., (Chemistry) : Inorganic & Physical Chemistry (205CH24)

First Edition : 2025

No. of Copies :

Published by:

Prof. V. VENKATESWARLU
Director, I/c
Centre for Distance Education,
Acharya Nagarjuna University

Printed at:

FOREWORD

Since its establishment in 1976, Acharya Nagarjuna University has been forging ahead in the path of progress and dynamism, offering a variety of courses and research contributions. I am extremely happy that by gaining 'A+' grade from the NAAC in the year 2024, Acharya Nagarjuna University is offering educational opportunities at the UG, PG levels apart from research degrees to students from over 221 affiliated colleges spread over the two districts of Guntur and Prakasam.

The University has also started the Centre for Distance Education in 2003-04 with the aim of taking higher education to the door step of all the sectors of the society. The centre will be a great help to those who cannot join in colleges, those who cannot afford the exorbitant fees as regular students, and even to housewives desirous of pursuing higher studies. Acharya Nagarjuna University has started offering B.Sc., B.A., B.B.A., and B.Com courses at the Degree level and M.A., M.Com., M.Sc., M.B.A., and L.L.M., courses at the PG level from the academic year 2003-2004 onwards.

To facilitate easier understanding by students studying through the distance mode, these self-instruction materials have been prepared by eminent and experienced teachers. The lessons have been drafted with great care and expertise in the stipulated time by these teachers. Constructive ideas and scholarly suggestions are welcome from students and teachers involved respectively. Such ideas will be incorporated for the greater efficacy of this distance mode of education. For clarification of doubts and feedback, weekly classes and contact classes will be arranged at the UG and PG levels respectively.

It is my aim that students getting higher education through the Centre for Distance Education should improve their qualification, have better employment opportunities and in turn be part of country's progress. It is my fond desire that in the years to come, the Centre for Distance Education will go from strength to strength in the form of new courses and by catering to larger number of people. My congratulations to all the Directors, Academic Coordinators, Editors and Lesson-writers of the Centre who have helped in these endeavors.

Prof. K. Gangadhara Rao
M.Tech., Ph.D.,
Vice-Chancellor I/c
Acharya Nagarjuna University.

M.Sc. INORGANIC & PHYSICAL CHEMISTRY –
PRACTICAL – I, SEMESTER-II
LAB SYLLABUS

A total Six (6) Experiments must be carryout taking minimum of ‘3’ in each section

LIST OF EXPERIMETNS:
SECTION-I: INORGANIC CHEMISTRY

Semimicro analysis of six radical mixtures containing one interfering radical and one less familiar cation each.

Interfering Anions : Oxalate, tartrate, phosphate, chromate.
Less familiar Cations : Thallium, molybdenum, thorium, zirconium, vanadium, uranium.
(Minimum three Mixtures)

SECTION-II: PHYSICAL CHEMISTRY

1) Potentiometric determination of Fe(II) with Cr(VI)
2) pH-metric determination of strong acid with strong base.
3) Conductometric titration of strong acid with strong base
4) Verification of Beers Law using potassium permanganate.

Reference Books:

1) Vogels Text Books of Qualitative analysis, Revised. J. asset, R.C. Denny, G.H. Jeffery and J. Mendhan. ELBS.
2) Synthesis and Characterisation of Inorganic Compounds, W.L.Jolly. Prentice Hall.
3) Practical Inorganic chemistry by G. Pass and H. Sutcliffe Chapman and Hall.
4) Practical Inorganic Chemistry by. K. Somasekhar Rao and K.N.K. VaniACHARYA

CONTENTS

S.No.	TITLE	PAGE No.
Qualitative Analysis (Semi-Micro Analysis)		
1	Introduction	1
2	Physical Tests	2
3	Identification of Anions	3
4	Removal of Interfering Radicals	4
5	Identification of Cations	5
	PHYSICAL CHEMISTRY MANUAL	
1	Potentiometric determination of Fe(II) with Cr(VI)	30
2	pH-metric determination of strong acid with strong base.	33
3	Conductometric titration of strong acid with strong base	39
4	Verification of Beers Law using Potassium Permanganate.	43

QUALITATIVE ANALYSIS

INTRODUCTION

Macro Analysis: The quantity of the substance employed is 0.1 to 0.5 g and the volume taken for analysis is about 20 ml.

Semi micro Analysis: In this, the quantities are reduced to 10 to 20 times when compared with macro analysis i.e. about 0.05 g and 1 ml solution.

Micro Analysis: In this, the quantities are reduced to 100 to 200 times when compared with macro analysis.

Note: The given unknown substance is a mixture of salts containing cations and anion. It is very essential on the part of the student to record all observations as and when they are made. It is found to be best recorded in three columns, experimental, observation and inference. The first column is a list of all tests to be made and may be kept filled in advance. Negative reactions should not be ignored and should be recorded.

General instructions and clues:

1. The apparatus used must be clean.
2. Add solutions in drop wise.
3. Whenever a reagent is added, shake the test tube gently and thoroughly.
4. The conditions prescribed for precipitation must be followed scrupulously. When a precipitate is obtained, digest the precipitate for coagulation and then centrifuge. Ensure complete precipitation of the ion concerned. The precipitate must be washed to remove the adhering metal ions of other groups. The first washings must be added to the centrifuge from which the precipitate was obtained.
5. If the volume of the solution at any stage becomes too large, it should be reduced by evaporation.
6. If original solution of the mixture is made in HCl, I groups is absent.
7. (a) For analysis from II group onwards, adjust the acidity as follows: Take the centrifugate of I group or in the absence of I group, take 2 ml of the original solution and add it to 2 ml of water.
   (b) If the original solution is made in water or in 6N HNO_3, after dilultion add 6 drops of 6N HCl.
8. While testing II and IV groups: Before passing H_2S through the entire solution, pass H_2S through a small portion of it separately. If a precipitate forms, pass H_2S through the bulk of the solution. If no precipitate forms, pass on to the next group with the bulk solution.
9. The centrifugate obtained after precipitation II and IV group metals by passing H_2S must be made free of dissolved H_2S before using it for further group.
10. (a) If III group is absent, take small portions of this solution (having NH_4Cl and NH_4OH) to find out the presence of IV, V and VI group cations.
    (b) If IV group is absent, take another portion of the solution and add $(NH_4)_2CO_3$ solution.
    (c) If V group is also absent, take the other portion and test6 for VI group.

SYSTEMATIC PROCEDURE FOR THE SEMI-MICRO ANALYSIS

Experiment	**Observation**	**Inference**
I. Physical tests:		
a. Nature of the substance	Crystalline or amorphous	
b. Odour: Smell of the mixture is noticed.	Smell of vinegar	May be acetate ion
	Smell of ammonia	May be ammonium
	Smell of H_2S	May be sulphides
c. Colour of the substance*:	Colour less	Absence of salts like Fe, Co, Ni, Cr, Mn etc.
	Blue	Hydrated Cu^{+2} satls, anhydrous
	Brown	PbO_2, Fe^{+3} salts, chromium, Nickel salts etc.
	Green	Hydrated Fe^{+2} salts, Ni^{+2} salts, some cr^{+3} salts and some cu^{+2} salts.
	Pink	Salts of cobalt.
	Yellow colour	Salts of Col, Hg, As, Sb
	Black	Sulphides of Ag, Pb, Hg, Cu, Sb, Ni, Cu, Fe or oxides of Mn etc
d. **Action of heat**: The substance is taken in a small ignition tube and heated gently first and then more strongly in a Bunsen flame.	A) Sublimation: On the upper walls of the test tube	
	(i) White sublimated is observed	May be ammonium salts, Hg(I) or Hg(II) chlorides, As(III), Sb(III), Se(IV) Oxides.
	(ii) Yellow sublimate is observed.	May be Sulphur, As(III) sulphide and Hg(I) or Hg(II) iodides.
	(iii) Black sublimate is observed.	May be Hg(I) or Hg(II) sulphides.

* It may not reflect in the mixture

Experiment	Observation	Inference
	B) Evolution of gases:	
	(i) Colourless and odourless CO_2 is observed which turns limewater to milky.	May be carbonates and organic compounds like oxalates.
	(ii) Light greenish Chlorine gas is evolved which turns starch-iodide paper blue.	May be chlorides.
	(iii) Reddish brown bromine vapours or violet iodine vapours are observed.	May be bromides or iodides.
	(iv) SO_2 is evolved.	May be sulphites, thiosulphates, sulphides.
	(v) NO_2 is evolved.	May be nitrates.
	(vi) Colourless, pungent ammonia is evolved.	May be ammonium salts.
	(vii) Oxygen is evolved.	May be chlorates, perchlorates, bromates, iodates etc.
	C. Substance chars with	
	(i) smell of burnt sugar.	May be tartarates.
	(ii) loss of carbon	May be oxalates.
	D. Change in colour	
	Yellow when hot white when cold	Zinc salts
(e) **Flame test**: Mix a small amount of the solid with two drops of Conc.HCl. Stil into paste with a platinum wire and introduce a little of the paste on the wire into the oxidizing region of the Bunsen flame.	Violet	Potassium
	Golden yellow	May be Na^+
	Brick red	Calcium
	Crimson red	Strontium
	Apple green	Barium
	Bluish green	Copper
	Flashes of green	May be Zn^{+2}, Mn^{+2}
f) Solubility: The solubility of the given compound is tested in water or dil HCl or dilHNO_3	Solubility is tested in water, dil HCl, dilHNO_3etc. aquaregia.	Presence of NH_4^+, K^+ or Na^+
	Soluble completely in water and the soluble portion will not give precipitation with Na_2CO_3.	Absence of I group cations.
	Soluble in dil HCl.	

Experiment	Observation	Inference
g) **Charcoal bead test:**		
Mix the substance with twice its bulk of anhydrous Na_2CO_3 of fusion mixture (Na_2CO_3+ K_2CO_3) and place it in a cavity of charcoal. Moisture is with a drop of water and heat it on the reducing flame with the help of blowpipe. The formation of bead incrustation dirt colour while hot and cold.	A) A metallic bead is formed.	
	1. White metallic	Ag^+
	2. Red flame	Cu
	3. Grey metallic particles	Fe, Co, Ni
	B) Incrustation with metal	
	1. White brittle method	Antimony
	2. Yellow, brittle metal	Bismuth
	C) Incrustation without metal:	
	1. White yellow when hot	Zinc
	2. White Garlic odour	Arsenic
	3. Brown	Cadmium

h. Borax bead test: A platinum wire is used for borax bead test. The free end of the platinum wire is coiled into a small loop. The loop is heated in the Bunsen flame until it is red hot and then quickly dipped into powdered borax. [$Na_2B_4O_7.10H_2O$], and heated until colourless and transparent. A minute quantity of substance is brought in contact with the hot bead and heated in the oxidizing flame. The colour is observed when the bead is hot and cold. The bead is heated in inner and outer flame and the colour is observed in hot and cold state.

Oxidising flame	**Reducing flame**	**Metal**
1. Green when hot, blue when cold	Colourless when hot and red when cold	Copper
2. Red when hot, yellows when cold	Colourless when hot and cold	Iron
3. Dark yellow when hot, green when cold.	When hot and cold green	Chromium
4. Violet when hot and cold	Colourless when hot and cold	Magnesium
5. Blue when hot and cold	Blue when hot and cold	Cobalt
6. Reddish brown when cold.	Blue when hot and cold	Nickel

II. Examination of volatile production on reaction with acid.

Experiment	Observation	Inference
1. **Reaction with dil.HCl**: The mixture is heated with dil HCl in a dry text tube	a) Brisk effervesence, with evolution of colour less, colourless gas. b) Colourless gas with penetrating smell of burning sulphur. c) Evolution of colourless gas with rotten egg smell and turns colour of lead acetate paper black. d) Evolution of brown fames with pungent colour e) Evolution of colourless gas with suffocating smell burning sulphur and yellowish precipetate of sulphur is deposited at the bottom of the test tube. f) Pale blue liquid is closed and brown fames are evolved	CO_3^{-2} (Carbonate) Or Bicarbonate(Hco_3) SO_3^{-2} (Sulphite) Sulphide (S^{-2}) Nitrate (NO_3^-) Thiosulphate($S_2O_3^{-2}$) Nitrite(NO_2^-)
2. Reaction with conc H_2SO_4: The mixture is heated with conc.H_2SO_4	a) Colourless fuming gas sides of the test tube appear oily. b) Colourless pungent gas c) Colourless pungent gas is evolved, some brown fumes are also evolved d) Dark violet fumes are evolved e) Pungent colourless (OR) light brown gas is evolved f) Colourless and odourless gas is evolved which burns with a blue flame at the month of the test tube. g) White fumes of boric acid on heating. h) Smell of vinegar i) Charring occurs immediately and smell of burnt sugar's observed. $CO+CO_2$ is evolved.	Fluoride(F^-) Chloride(Cl^-) Bromide(Br^-) Iodide(I^-) Nitrate(NO_3^-) Oxalate($C_2O_4^{-2}$) Borate (BO_3^{-3}) Acetate Tartarate($C_4H_4O_6^{-2}$)

III. Confirmatory Tests:

Experiment	**Observation**	**Inference**
1. Heat the mixture with dil.HCl or dil.H_2SO_4in dry test tube	Colourless gas is evolved which when passed into limewater turns milky.	Carbonate(CO_3^{-2})
2. To the excess solution of salt mixture, add a solution of $MgSO_4$. boil the solution.	A white precipitate is formed.	Bicarbonate (HCO_3^-)
3. Heat the mixture with dil.Hcl or dil.H_2SO_4 in a dry test tube.	Evolution of colourless gas with suffocating odour of burning sulphur. The evolved gas turns potassium dichromate paper green.	Sulphite (SO_3^{-2})
4. To the neutral or acid solution, $AgNO_3$ solution is added. (OR)	Black precipitate is formed.	Sulphide (S^{2-})
To the given mixture lead acetate solution is added.	Black precipitate is formed.	Sulphide (S^{2-})
5. To the solution of the mixture, a saturated solution of $FeSO_4$ acidified with dil. acetic acid or with dil.H_2SO_4 is added. (OR)	A brown ring is formed. $FeSO_4.NO$	Nitrite (NO_2^-)
To the mixture $AgNO_3$ solution is added.	White crystalline precipitate of silver nitrite is formed.	Nitrite (NO_2^-)
6. A small amount of the substance is rubbed with oxalic acid with a few drops of water between fingers. (OR)	Smell of vinegar.	Acetate (CH_3COO^-)
To the solution of mixture, Conc.H_2SO_4 and CH_3OH are added and heated. It is then poured into water.	Fruity odour is obtained.	Acetate (CH_3COO^-)
7. To the solution of mixture, lead acetate solution is added. (OR)	At first no change is observed, but on further addition of the reagent a white ppt. is formed.	Thiosulphate ($S_2O_3^{2-}$)
To the mixture, $FeCl_3$ solution is added.	A dark violet colour appears.	Thiosulphate ($S_2O_3^{2-}$)

Experiment	Observation	Inference
8. To the given mixture conc.H_2SO_4 is added and heated. (OR)	Colourless pungent gas evolved. A glass rod dipped in NH_3 is brought near the test tube mouth. White dense fumes are observed.	Chloride (Cl^-)
The given mixture is heated with conc.H_2SO_4 and MnO_2.	Greenish yellow gas is evolved.	Chloride (Cl^-)
9. Heat the mixture with $K_2Cr_2O_7$ and conc.H_2SO_4.	Reddish brown (CrO_2Cl_2) vapours are evolved. These vapours when passed into the test tube containing NaOH and lead acetate solution a yellow ppt is formed.	Chloride (Cl^-)
10. The given mixture is heated with Conc.H_2SO_4 and MnO_2.	Brown vapours of bromine are evolved.	Bromide (Br^-)
11. The given mixture is heated with Conc.H_2SO_4 and MnO_2.	Dark violet fumes are evolved. These violet vapours turns starch paper blue.	Iodide (I^-)
12. To the given mixture copper turnings and conc.H_2SO_4 are added and heated.	Deep brown fumes are evolved.	Nitrate(NO_3^-)
13. To the mixture diphenylamine is added and heated gently. Cooled it and three drops of alcohol are added. (OR)	Blue colour chain is observed.	Oxalate ($C_2O_4^{2-}$)
To the solution of mixture dil.CH_3COOH and $CaCl_2$ solution are added.	A white ppt. which decolourises $KMnO_4$ is observed.	Oxalate ($C_2O_4^{2-}$)
14. To a little mixture in a porcelain dish a little conc.H_2SO_4 and C_2H_5OH are added and burned. (OR)	These vapours burned with green edged flame.	Borate (BO_3^{3-})
A small amount of mixture is taken and made paste with CaF_2 and little conc.H_2SO_4. The paste is taken on a glass rod and brought to the edge of the flame.	Green flame is observed.	Borate (BO_3^{3-})

Experiment	Observation	Inference
15. To the mixture lead acetate is added.	Yellow ppt soluble in HNO_3 and insoluble in CH_3COOH is formed.	Chromate ($Cr_2O_4^{2-}$)
16. The substance is neutralized with ammonia sol. And 1 ml of CH_3COOH is added. Then $AgNO_3$ solution is added.	Brown ppt. is formed.	Chromate (CrO_4^{2-})
17. To the solution of mixture, dil.CH_3COOH and $CaCl_2$ solution are added.	A white ppt. is formed.	Fluoride (F^-)
18. The mixture is boiled with conc.HNO_3.	A canary yellow ppt. is formed. The ppt. is soluble in NH_4OH and alkaline hydroxide solution.	Phosphate (PO_4^{3-})
19. To the solution of mixture dil.HCl or HNO_3 and $BaCl_2$ solution are added.	A curdy white ppt. is formed. The ppt. is insoluble in conc. acid.	Sulphate (SO_4^{2-})
20. To the solution of mixture, equal amounts of saturated manganese(II) sulphate solution and 1M H_2SO_4 are added.	A red colour is observed. On concentration the solution brown MnO_2 (hydrated) separates.	Bromate (BrO_3^-)
21. To the solution of mixture barium chloride solution is added.	White ppt is observed. The ppt is sparingly soluble in hot water and in dil.HNO_3, but insoluble in alcohol. The ppt is washed well and treated with sulphurous acid sol and 1 to 2 ml of chloroform. Violet colouration is observed.	Iodate (IO_3^-) Iodate (IO_3^-)
22. To the solution of mixture, Mercuric(II) nitrate solution is added.	White ppt. is observed.	Iodate (IO_3^-)
23. To the neutral solution of the mixture, a solution of cadmium sulphate in conc. ammonia solution is added.	A white crystalline ppt is formed.	Perchlorate (ClO_4^-)

Experiment	Observation	Inference
24. To the solution of mixture, potassium chloride or ammonium chloride solution is added.	A white ppt. is formed. The ppt. is insoluble in alcohol.	Perchlorate (ClO_4^-)
25. To the solution of mixture, lead nitrate or lead acetate solution is added and boiled.	Brown coloured ppt is observed.	Hypochlorite (OCl^-)
26. To the solution mixture, silver nitrate solution is added.	A white ppt is formed and the ppt is soluble in excess of the cyanide solution.	Cyanide (CN^-)
27. To the solution of mixture cobalt acetate is added.	Blue colouration observed due to the formation of a complex. The colour is intensified by the addition of ethanol.	Cyanate (OCN^-)
28. Thiocyanates: To the solution of mixture, silver nitrate solution is added.	A curdy white ppt. is formed. The ppt. is soluble in ammonia and insoluble in nitric acid.	Thiocyanate (SCN^-)
29. To the solution of mixture, cadmium acetate solution is added.	A white gelatinous ppt. is formed. The ppt is insoluble in boiling water but readily soluble in warm acetic acid. (Tartarates give no ppt.)	Citrate ($C_6H_5O_7^{3-}$)

Confirmatory tests for anions with sod. Carbonate extract:

One part of the given substance is mixed with 2to3 parts by weight of sodium carbonate and 15 ml of distilled is added and boiled for about 10 to 15 minutes in a beaker. Now filtered it, the fitrate is called sodium carbonate extract.

$$XY + Na_2CO_3 \longrightarrow \underset{\text{Insoluble}}{XCO_3} + \underset{\text{Soluble in}}{Na_2Y}$$

water Where X and Y are cations and anions respectively.

Experiment	**Observation**	**Inference**
1. Tests for Halogens: The sod. Carbonate extract is neutralized with dil.HNO_3 and 3 ml of $AgNO_3$ solution is added.	a. A white ppt of AgCl is formed which is soluble in ammonia solution. b. A pale yellow ppt. of AgBr is formed and is hardly soluble in ammonia solution. c. Yellow ppt. is obtained which is insoluble in ammonia solution.	Chloride (Cl^-) Bromide (Br^-) Iodide (I^-)
2. The sod. Carbonate extract is neutralized with dil.H_2SO_4 and freshly prepared $FeSO_4$ solution is added. Then keeping the test tube in an inclined position, conc.H_2SO_4 is added from the walls of the test tube.	Brown ring of $FeSO_4.NO$ is formed at the junction of two liquids.	Nitrate (NO_3^-)
3. The sod. carbonate extract is acidified with CH_3COOH and $CaCl_2$ solution is added. The ppt is dissolved in dil.H_2SO_4 and warmed. To it few drops of acidified $KMnO_4$ is added.	A whit ppt of CaC_2O_4 is formed. The colour of $KMnO_4$ is discharged.	Oxalate ($C_2O_4^{2-}$)
4. About 10 ml of extract is heated with 0.5 ml of C_2H_5OH and H_2SO_4 in a boiling test tube. The expelled vapours are brought near the flame.	The vapours burn with green edged flame.	Borate (BO_3^{3-})
5. The sod. Carbonate extract is neutralized with dil.HCl and neutral $FeCl_3$ solution is added.	Deep colouration is formed. On boiling it becomes brownish red ppt.	Acetate (CH_3COO^-)
6. The sod. carbonate is neutralized with dil.HNO_3. Then Conc.HNO_3 and ammonium molybdate are added and heated.	A canary yellow ppt is formed.	Phosphate (PO_4^{3-})
7. To the sod. carbonate dil HCl is added to neutralize and then $BaCl_2$ solution is added.	White ppt. is formed. The ppt is insoluble in Conc. HCl	Sulphate (SO_4^{2-})

Experiment	Observation	Inference
8. The sod. carbonate extract is acidified with dil.HNO_3 and $AgNO_3$ solution is added in excess. This is heated in a boiling water bath.	A brilliant silver mirror is formed.	Tartarate ($C_4H_4O_6^{2-}$)
9. The sod. carbonate extract is neutralized with HNO_3. Now it is heated with $NaNO_2$ is added.	Whit ppt. of AgCl is formed	Chlorate (ClO_3^-)

(C) *Special ions:*

Experiment	Observation	Inference
1. To the neutral solution of mixture, $AgNO_3$ solution is added.	Yellow colour ppt. Brown colour ppt	Arsenite(AsO_3^{3-}) Arsenate(AsO_4^{3-})
2. To the solution of mixture, ferrous sulphate and sulphuric acid are added.	The solution becomes yellow.	Permangate (MnO_4^{4-})
3. To the solution of mixture, lead acetate solution is added.	Yellow ppt is formed. The ppt turns white or pale yellow on standing	Vanadate (VO_3^-)
4. To the solution of mixture, potassium hexacyanoferrate(II) solution is added.	A reddish brown ppt is formed. The ppt is insoluble in dilute mineral acids but soluble in solutions of caustic alkalis and ammonia.	Molybdate (MoO^{4-})
5. To a solution of mixture, ferric chloride solution and acid are added.	Prussian blue ppt is formed.	Ferrocyanide ion $[Fe(CN)_6]^{4-}$
6. To a solution of mixture, ferric chloride solution is added.	Brown colouration is observed.	Ferricyanide ion $[Fe(CN)_6]^{3-}$

Removal of interfering radicals: Oxalate, Borate, Fluoride, Phosphate, tartarate, chromate, Citrate in are known as interfering radicals. Their presence in the mixture stands in the usual way of analysis of basic radicals after second group. Actually salts of these radicals are soluble in acid medium but are insoluble in neutral or alkaline medium. Upto II group the medium remains acidic, hence they are not precipitated and thus they do not interfere. But in and after III group the medium is made alkaline by the addition of NH_4OH in which majority of the salts of these interfering radicals are insoluble. So in the III group oxalates, Phosphates, fluorides, borates etc of metals of III group and subsequent groups get precipitated. The hydroxides of the III group metals are also precipitated. In this way the normal procedure of analysis will be disturbed. Therefore it is essential to remove the interfering radicals before adding NH_4OH for the test of IIIrd group and subsequent group radicals.

Removal of oxalate: Take 2gm of the mixture in a porcelain dish and heat it strongly for 5-10 minutes. Now add 2-4 ml of con.HNO_3 and evaporate to dryness. Repeat the process four to five times when all oxalic acid gets oxidized to CO_2. Oxalate can also be removed from III group precipitate in the same manner described above.

Removal of Tartrate: Take 2gm of the mixture in a porcelain dish and heat strongly for 5-10 minutes. Now add 2-4 ml of Con.HNO_3 and evaporate to dryness. Repeat the process four or five times till all the tartarate is removed.

Removal of Borate: Take 2g of the mixture in a porcelain dish and add 2-4ml of con HCl. Evaporate the solution to almost dryness. Repeat this operation five to six times. The residue is dissolution little con HCl, diluted with water and can be used as the original solution. It can be removed form the IIIrd group precipitate in the manner described above.

Removal of fluoride: Fluoride is also removed by the same method as borate forming hydrofluoric acid which volatilizes. It can be removed from the III group precipitate in the manner described above.

Removal of chromate: Chromate can also be removed by the same above method.

Removal of Phosphate: The filtrate of III group is boiled to remove H_2S. Two drops of conc HNO_3 are added to convert ferrous salt into ferric one. Now NH_4Cl and NH_4OH (excess) are added till a clear smell of ammonia is obtained. If no ppt is obtained, then there is no need of removing phosphate. Now in this solutions containing ppt, sodium acetate and acetic acid are added in excess till the smell of acetic acid is noticed. If whole of the ppt dissolves then III group is supposed to be absent, if not then proceed as follows:

<table>
<tr>
<td rowspan="3"><u>Residue:</u>
III groups is present. Test as usual. If no residue is left behind III group is usually absent.</td>
<td colspan="3"><u>Filtrate:</u> Now the filtrate or the total solution in a beaker is taken and neutral $FeCl_3$ solution is added slowly without shaking until tea colour is obtained. Boiled for 5 to 10 minutes and filter.</td>
</tr>
<tr>
<td colspan="2"><u>Filtrate:</u> NH_4Cl and NH_4OH (excess) is added till lit smells of ammonia and filtered.</td>
<td rowspan="2"><u>Residue:</u> It is rejected.
$FePO_4$,
$Fe(OH)_2CH_3COO$
Basic ferric acetate</td>
</tr>
<tr>
<td><u>Filtrate:</u> Test the 4th and subsequent group radicals as usual.</td>
<td><u>Residue:</u> Reject it.</td>
</tr>
</table>

Treatment of Insolubles

Substances which are not soluble in conc. HCl (or HCl + HNO_3) are termed as insolubles. The insoluble materials met with commonly in mixtures are sulphates of Sr, Ba, Pb, some sulphides, particularly SnS_2 (mosaic gold), ignited oxides like Al_2O_3, Cr_2O_3, Fe_2O_3 and phosphates of some tetravalent metals like Zr.

On treating the unknown with HCl to prepare the solution for cation analysis, only the soluble dissolve. Insolubles and any chlorides of cations of group I remain in the residue. The residue is examined ;for group I ;using the following reagents in order- hot water, aq.NH_3, HCl, HNO_3. Any residue left over has to be analysed by the special procedure for insolubles.

Procedure for analysis of an insoluble

The insoluble residue is dried and fused on a nickel foil with small bit of solid NaOH and a crystal of KNO_3 and cooled. Placed the foil in a crucible or beaker and added 2 cc of 5% Na_2CO_3 and boiled, filtered.

<table>
<tr>
<td rowspan="2"><u>Residue</u>: Warmed with a little dil. HNO_3 and filtered. Rejected any residue. The solution tested for groups III and IV.</td>
<td colspan="2"><u>Filtrate:</u> Neutralised with HCl and evaporated to dryness. Digested with HCl, filtered.</td>
</tr>
<tr>
<td><u>Residue</u>: SiO_2</td>
<td><u>Filtrate</u>: Tested for cations of group II and III.</td>
</tr>
</table>

Notes:

1. Fusion with NaOH opens epoxides, sulphides, sulphates and phosphates. On boiling with Na_2CO_3 group V metals are precipitated as carbonates. The weakly negative amophoteric metals eg. Zr are precipitated as hydroxides. Hydroxides and carbonates are found in the residue. The solution contains anions of the amphoteric metals and anions like silicate and phosphate.
2. In the case of insoluble residue containing only barium or strontium sulphate fusion with fusion mixture (Na_2CO_3 + K_2CO_3) is enough. Fusion may be done in a broken bit of porcelain. The mass is leached with water and the residual carbonate is dissolved in dil. HCl and tested for the metal ion.

$$BaSO_4 + K_2CO_3 \longrightarrow \underset{\text{(WATER SOLUBLE)}}{K_2SO_4} + BaCO_3$$

(RESIDUE)

Classification of cations into groups:

Group	**Group Reagent**		**Cations included**	**Precipitate with colour**
I	Cold dil.HCl		Hg_2^{2+}, Ag^+, Pb^{2+}, Tl^+, W^{6+}	Hg_2Cl_2, AgCl, $PbCl_2$, TlCl(All white) H_2WO_4(light yellow)
IA	Hydrazine hydrochloride		Se^{4+}, Se^{6+}, Te^{4+}	Metallic Se (Red), Metallic Te (Blue black)
II	Dil. HCl +H_2S	IIA	Hg^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Bi^{3+}	HgS, CuS, PbS (All black), CdS (Yellow), Bi_2S_3 (Brownish black)
	KOH	IIB	As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Sn^{4+}, Mo^{6+}	As_2S_3, As_2S_5 (yellow), Sb_2S_3, Sb_2S_5 (orange red) SnS (brown) SnS_2(yellow), MoS_3 (Brown)
III	Solid NH_4Cl+ NH_4OH		Fe^{3+}, Al^{3+}, Cr^{3+}, Ce^{4+},Zr^{4+},	$Fe(OH)_3$ (Red brown), $Al(OH)_3$ (Gelatinous white) $Cr(OH)_3$ (Bluish green
			Ti^{4+}, $V^{5+}(VO_3^-)$, U^{6+} (UO_2^{2+})	$Zr(OH)_4$, $Ti(OH)_4$ (Both white),
				$Ce(OH)_4$, $(NH_4)_2U_2O_7$ (both yellow), NH_4VO_3 (pale blue)
IV	Solid NH_4Cl+		Co^{2+}, Ni^{2+}, Mn^{2+},	CoS, NiS, Tl_2S (All black), ZnS(dirty white),
				MnS (Flesh coloured)
	NH_4OH +H_2S		Zn^{2+}, Tl^+(traces)	
V	Solid NH_4Cl + NH_4OH +$(NH)_2CO_3$		Ba^{2+}, Sr^{2+}, Ca^{2+}	$BaCO_3$, $SrCO_3$, $CaCO_3$ (All white)
VI	–		NH_4^+, Mg^{2+}, Li^+, Na^+, K^+	Flame test: Li (Crimson red), Na (Golden yellow), K (Lilac)

Test for NH_4^+:

Since many ammonium salts are added during the course of analysis, the ion has to be tested in the given mixture before proceeding to the systematic cation analysis.

(i) NaOH Test: To 0.5 ml of the original solution, 0.5 ml of NaOH solution is added in a test tube and heated. The evolved gas is smelled. Ammonia gas smell indicates NH_4^{4+}.

(ii) Nessler's reagent Test: To a few drops of the original solution in a test tube, a few drops of Nessler's reagent are added. Brick red precipitate indicates NH_4^+.

Preparation of original solution:

Prepare original solution of the mixture trying its solubility in the following solvents in the order given:
1. Distilled water 2. Dil. HNO_3 3. Conc. HNO_3 4. Conc. HCl 5. Aquaregia (1:3 conc.HNO_3 : Conc.HCl)

Separation of cations into groups

To 4 ml of original solution in a centrifuge tube, dil.HCl is added drop wise. If a precipitate is formed, dil. HCl is added till precipitation is completed, cooled and centrifuged. To the residue 6 drops of water are added, shaken, cooled and centrifuged again. This centrifuge is added to the one already obtained.

<table>
<tr>
<td rowspan="6"><i>Residue</i>:
I groups cations are present.
Analysed by I group table.</td>
<td colspan="7"><i>Centrifugate</i>: A few crystals of hydrazine hydrochloride are added, heated on water bath and centrifuged.</td>
</tr>
<tr>
<td rowspan="5"><i>Residue</i>: IA groups cations are present.
Analysed by IA group table.</td>
<td colspan="6"><i>Centrifugate</i>: 2 drops of 6% H_2O_2 are added, heated, diluted with 2 ml water and H_2S is passed and centrifuged.</td>
</tr>
<tr>
<td colspan="2">Residue: IIA & IIB groups cations. Boiled with 1ml of 2N KOH and centrifuged.</td>
<td colspan="4"><i>Centrifugate</i>: H_2S is boiled off and 3 to 4 drops of Conc.HNO_3 is added. Boiled it again. (Test for the presence of Fe^{3+} by taking 1 drop of the solution and adding 2 drops of NH_4SCN solution. Deep red colouration indicates Fe). To the bulk of solution, 2 drops of $FeCl_3$ and 5 drops of saturated NH_4Cl are added. The solution is heated without boiling. To the hot solution 1:1 NH_4OH (excess) is added and centrifuged.</td>
</tr>
<tr>
<td rowspan="3"><i>Residue</i>:
IIA group cations.
Analysed by IIA group table.</td>
<td rowspan="3">Centrifugate:
IIB group cations.
Analysed by IIB table.</td>
<td rowspan="3"><i>Residue</i>:
III group cations.
Analysed by III group table.</td>
<td colspan="3"><i>Centrifugate</i>: 4 drops of NH_4OH is added, H_2S gas is passed till precipitation is completed and centrifuged.</td>
</tr>
<tr>
<td rowspan="2"><i>Residue</i>: IV group cations.
Analysed by IV group table.</td>
<td colspan="2"><i>Centrifugate</i>: H_2S is boiled off and concentrated to 2 ml. A few drops of NH_4OH and 10 to 15 drops of saturated $(NH_4)_2CO_3$ are added. (If a precipitate is formed, a few more drops of $(NH_4)_2CO_3$ are added so that precipitation is completed). Heated in water bath and centrifuged.</td>
</tr>
<tr>
<td><i>Residue</i>: V group cations.
Analysed by V group table.</td>
<td><i>Centrifugate</i>:
Analysed for VI group cations.</td>
</tr>
</table>

Analysis of cations including the less familiar elements

ANALYSIS OF GROUP –I

To 4ml of the original solution, 2ml of dil HCl is added. Boiled and cooled. Centrifuge the cold solution. Washed the precipitate with cold water. Combine washings and centrifugate and save it for analysis of further groups.

<table>
<tr><td colspan="5"><i>Residue</i>: Chlorides of Pb^{+2}, Hg_2^{2+}, Ag^{+}, Tl^{+} and WO_2. The residue is boiled with 3 ml water, centrifuged the hot solution rapidly and the clear solution is removed immediately. (If the residue is completely soluble in water Hg_2^{2+}, W^{6+} and Ag^{+} are absent.</td></tr>
<tr><td colspan="3"><i>Residue</i>: Hg_2Cl_2, AgCl, WO_2; :Washed twice with hot water to remove any Pb^{+2}, Tl^{+} chlorides. Washings are rejected. ½ c.c. of dil.aq.NH_3 is added, warmed and centrifuged.</td><td colspan="2"><i>Centrifugate</i>: $PbCl_2$ and TlCl. 2 drops of conc.H_2SO_4 are added and heated to fumes. Then 1 c.c. of water is added cautiously, stirred and centrifuged</td></tr>
<tr><td rowspan="2"><i>Residue</i>: Black
Three drops of conc. HCl and a drop of conc. HNO_3 are added, heated and centrifuged. To the clear centrifugate, 3 drops of $SnCl_2$ are added. White or grey ppt.
Mercury</td><td colspan="2"><i>Centrifugate</i>: $[Ag(NH_3)_2]Cl$ and ammonium tungstate
Dil. HCl was added drop wise till a ppt begins to form. It is redissolved with drops of aq.NH_3. Two drops of KI are added and centrifuged.</td><td rowspan="2"><i>Residue</i>: Whit $PbSO_4$
5 drops of NH_4Oac are added and warmed. 2 drops of dil HOAc and 2 drops of K_2CrO_4 are added. A yellow ppt is observed.
Lead</td><td rowspan="2"><i>Centrifugate</i>: Tl_2SO_4
Just neutralized with aq.NH_3 and 2 drops of KI solution and 2 drops of $Na_2S_2O_3$ are added.
Yellow ppt. TlI indicates Thallium
Flame colour - green</td></tr>
<tr><td><i>Residue</i>: Yellow AgI insoluble in aq. NH_3 indicates
Silver</td><td><i>Centrifugate</i>: Evaporated to half the bulk and 2 drops of $SnCl_2$ and 2 drops of conc. HCl are added and warmed. Blue ppt. shows
Tungsten</td></tr>
</table>

Spot tests for Tl:

1. To one drop of the solution, one drop of $Na_3[Co(NO_2)_6]$ solution is added. A light red precipitate of $Tl_3[Co(NO_2)_6]$ forms.
2. To one drop of the solution, one drop of $K_2Cr_2O_7$ solution is added. Yellow precipitate of Tl_2CrO_4 insoluble in dil. HNO_3 is formed.

Analysis of Group - I_A

To the centrifugate from I group, a few crystals of hydrazine hydrochloride are added and heated on water bath. Centrifuged, washed the residue with water and combine washings with centrifugate.

<table>
<tr><td colspan="5"><i>Residue</i>: Add two drops of conc. HCl and equal amount of bromine water. Boiled and 5 drops of saturated NH_4Cl is added and centrifuged.</td><td rowspan="5"><i>Centrifugate</i>: Examined for further groups.</td></tr>
<tr><td rowspan="4"><i>Residue</i>:
Orange yellow crystals $(NH_4)_2[PtCl_6]$
Platinum</td><td colspan="4"><i>Centrifugate</i>: Add 2-3 crystals of oxalic acid, boiled and centrifuged.</td></tr>
<tr><td rowspan="3">Residue:
Brown ppt.
Gold</td><td colspan="3"><i>Centrifugate</i>: Add aq.NH_3. Red ppt is formed. Pd is present. Add a slight excess of NH_3 and then dil. HCl and centrifuge.</td></tr>
<tr><td rowspan="2"><i>Residue</i>: Yellow crystals of $[Pd(NH)_3Cl_2]$. Boiled with 5 drops of conc. HCl and one drop of conc.HNO_3. Extracted with minimum 1N HCl and 2 drops of dimethyl glyoxime reagent.
Yellow ppt
Palladium,</td><td colspan="2"><i>Centrifugate</i>: A few crystals of $NH_2OH.HCl$ are added , warmed and centrifuged.</td></tr>
<tr><td><i>Residue</i>:
Red Crystalline powder shows
Selenium</td><td><i>Centrifugate</i>: A crystal of N_2H_4. 2HCl was added and boiled. A blue-black colour crystalline ppt shows
Tellurium</td></tr>
</table>

ANALYSIS OF GROUP II [A and B- Copper and tin groups Separation of copper and Tin groups

To the centrifugate from group I, one drop of 6% H_2O_2 is added. Heated and dilute to about 3 c.c. Transferred to a small conical flaks, neutralized with aq NH_3 (litmus) and 1 to 2 c.c. of dil.HCl is added. Heated and saturated with H_2S. It is preferable to close the flask with a one- holed stopper and introduce the H_2S delivery tube through it so that the tip is above the solution level. This enables to build up a slight pressure of H_2S. The flask should be well shaken. The precipitate is removed by centrifugation, diluted the centrifugate to 5 c.c. Warmed, saturated with H_2S again and centrifuged. Washed the residue with 1 c.c. water and added washings to centrifugate.

<table>
<tr><td colspan="2">*Residue*: Contains sulphides of copper and tin groups. Boiled with 1 to 2 c.c. of 2N NaOH, heated and centrifugated. Washed residue with water and combined the centrifugate and washings.</td><td rowspan="2">*Centrifugate*: Examined for group group III and subsequent groups.</td></tr>
<tr><td>*Residue*: copper group sulphides.
This residue is used for the analysis of II_A group.</td><td>*Centrifugate*: Neutralised with dil.HCl (litmus), heated and centrifuged. Washed the precipitate. The centrifugate and washings are discarded. The precipitate is used for the analysis of II_B group.</td></tr>
</table>

Analysis of group - II_A

The ppt is washed once with 1 c.c. of water to remove alkali. Washings are discarded. 1.5 c.c. of dil. HNO_3 is added to residue. Boiled the solution, 2 drops of dil. H_2SO_4 are added and centrifuged.

<table>
<tr>
<td colspan="2"><i><u>Residue</u></i>: HgS and $PbSO_4$. Washed with 1 c.c. of water. Centrifuged and washings are discarded. 5 drops of saturated NH_4OAc , heated and centrifuged.</td>
<td colspan="2"><i><u>Centrifugate</u></i>: Nitrates of Cu^{2+}, Cd^{2+} and Bi^{3+}. Slight excess of ammonia (smell) is added in drop wise. Heated and centrifuged.</td>
</tr>
<tr>
<td><i><u>Residue</u></i>: 3 drops of conc. HCl are added and heated.
Diluted to ½ c.c. with water and 2 drops of $SnCl_2$ are added.
White or grey ppt. indicates
Mercury</td>
<td><i><u>Centrifugate</u></i>:
1 drop of dil. HOAc and 2 drops of K_2CrO_4.
Yellow ppt. shows
Lead</td>
<td><i><u>Residue</u></i>: Dil. HCl is added drop wise till the residue is dissolved and 3 drops of stannite solution is added.
Black and white ppt shows
Bismuth</td>
<td><i><u>Centrifugate</u></i>: Deep blue if Cu is present.
Divided into two portions.
(i) Dil. HOAc is added drop wise till pale blue and then 2 drops of $K_4[Fe(CN)_6]$ are added.
Reddish brown ppt indicates
Copper
(ii) To another part, drops of KCN are added till the solution become colourless. Diluted with equal volume of water. H_2S is passed.
Yellow ppt indicates
Cadmium</td>
</tr>
</table>

Sodium stannite solution: Sodium hydroxide solution is added drop wise to 0.5 ml of $SnCl_2$ solution. A white precipitate is formed and continued the addition of NaOH till the precipitate is dissolved.

Analysis of group II_B

The ppt is washed with NH_4Cl solution. 10 drops of conc. HCl are added, stirred and heated for a minute. 10 drops of water are added. Stirred and centrifuged.

<table>
<tr>
<td colspan="2"><i>Residue</i>:As_2S_3 and MoS_3. 5 drops of saturated $(NH_4)_2CO_3$ solution is added. Stirred well and centrifuged.</td>
<td rowspan="2"><i>Centrifugate</i>: Contains Tin and Antimony
Divide centrifugate into several portions.
i) To 5 drops of the centrifugate, a small quantity of iron filings or Zn dust is added. Warmed to dissolve the metal and 3 drops of $HgCl_2$ is added.
White Hg_2Cl_2 or grey Hg indicates
Tin
ii) To 5 drops of the centrifugate, a few crystals of $NaNO_2$ are added and shaken. 5 drops of Rhodamine B reagent is added.
Lavender colour indicates
Antimony
iii) To 5 drops of centrifugate, crystals of oxalic acid are added to saturation. The solution is diluted and H_2S is passed.
Orange precipitate indicates
Antimony</td>
</tr>
<tr>
<td><i>Residue</i>: Dark brown MoS_3. 3 drops of conc. HCl and 2 drops of bromine water are added.
The solution is boiled to expel the excess bromide. The solution is then diluted and 5 drops of 10%KCNS,
3 drops of $SnCl_2$, 10drops of amyl alcohol were added and shaken.
Formation of red alcohol layer indicates
Molybdenum</td>
<td><i>Centrifugate</i>: The centrifugate is acidified.
(i) To one portion, 5 drops of saturated solution of $(NH_4)_2CO_3$ are added and shaken. Acidified the centrifugate carefully with dilHCl. Yellow ppt is formed indicating As.
(ii) To another portion, 3 drops of $AgNO_3$ are added and then aqNH_3 drop by drop. Reddish brown precipitate is formed indicating As.
(iii) To another portion a piece of Zn and 5 drops of dil H_2SO_4 are added. The test tube plugged loosely with cotton and placed $HgCl_2$ paper over it.
Yellow or reddish stains indicates
Arsenic</td>
</tr>
</table>

Spot test for Molybdenum: To a drop of molybdate solution, a drop of 10% KSCN is added. Then a drop of Conc.HCl and a drop of $SnCl_2$ are added. Red spot indicates Mo.

Before proceeding to the analysis of III group cations, the interfering radicals should be removed.

Analysis of group III [iron group]

H_2S is boiled off from the centrifugate from group II. 2 drops of conc. HNO_3 are added and boiled. A drop of the solution is tested for the presence of Fe^{+3} with KSCN. Two drops of $FeCl^{+3}$ are added to the bulk of the solution and then five drops of saturated NH_4Cl solution. Heated without boiling. To the hot solution, aq.NH_3 is added to very slight excess. Centrifuged, washed the residue with small amounts of NH_4Cl solution and washings are added to centrifuge. The centrifugate is examined for groups IV and on.

<table>
<tr><td colspan="7">Residue: Hydrated oxides of various metals of the group. Dissolved in minimum amount of dil HCl, about 50 mg of oxalic acid crystals are added, digested to hot and centrifuged.</td></tr>
<tr><td colspan="2">Residue: Oxalates of Th and Ce 1 c.c. of saturated $(NH_4)_2C_2O_4$ are added, boiled and centrifuged.</td><td colspan="5">Centrifugate: Neutralised with aq.NH_3 and digested to hot for a few minutes. Centrifuged and discarded the sol. The residue is washed with dil NH_4Cl solution and washings are discarded. Suspended in 1 c.c. of water in a boiling tube and about 50 mg Na_2O_2 are added. Boiled till effervescence ceases, centrifuged, washed the residue with water and combined washings with centrifugate.</td></tr>
<tr><td rowspan="4">Residue:
1</td><td rowspan="4">Centrifugate:
2</td><td rowspan="4">Residue: Hydrated oxides of Tl, Fe, Ti, Zr and Mn. Redissolved in dil HCl, boiled and divided into several test potions.
i. To the first portion, 2 drops of KI and then $Na_2S_2O_3$ (in drops) are added. Yellow ppt of TlI indicates
Thallium
ii. To the second portion, syrupy phosphoric acid is added in dropwise just to decolourise the iron. 2 drops of 6% H_2O_2 and 2 drops of dil H_2SO_4 are added. Orange colour indicates Titanium
Ppt indicates Zirconium. Centrifuged.</td><td colspan="4">Centrifugate: Chromate, aluminate, uranate, vanadate and beryllate.
Acidified with dil HNO_3, 5 drops of $Pb(NO_3)_2$ are added and then about 200 mg of NH_4OAc crystals are added, stirred well and centrifuged.</td></tr>
<tr><td rowspan="3">Residue: $PbCrO_4$ and $Pb(VO_3)_4$
Dissolve in 10 drops of dil.HNO_3 and cooled. 10ml of amyl alcohol & 3 drops of 6% H_2O_2, shaken. Blue alcohol layer indicates
Chromium
Reddish brown aq. Layer shows vanadium. The aq.</td><td colspan="3">Centrifugate: Nitrates of Pb^{+2}, Al^{3+}, Be^{2+}, UO_2^{+2}
3 drops of dil. HCl are added and H_2S is passed. Centrifuged and precipitated PbS is rejected. The centrifugate is boiled to expel H_2S. Cooled and saturated $[(NH_4)_2]CO_3$ is added drop wise carefully. Boiled for a minute and centrifuged.</td></tr>
<tr><td colspan="2">Residue: Basic carbonates & hydroxides of Al and Be.
Dissolved in the minimum volume of dil.HCl, 2 drops of $Na_2S_2O_3$ are added. Warmed and centrifuged.</td><td rowspan="2">Centrifugate:
Complex of uranyl carbonate
Evaporated to a small volume, acidified with dil.HCl (to remove any ppt) and 2 drops of $K_4[Fe(CN)_6]$ are added. Brown ppt turns yellow on adding NaOH indicates</td></tr>
<tr><td>Residue:
$Al(OH)_3$
Confirmed by Thenard’s blue test
Aluminium</td><td>Centrifugate:
Beryllium
Confirmed by
Quinalizarin test
Beryllium</td></tr>
</table>

		Residue: White Zirconium phosphate **Zirconium** Centrifugate: 20 mg of $Na_2S_2O_3$ is added and heated. White ppt of $Ti(OH)(PO_4)$ **Titanium** iii. To the third portion, a drop of conc. H_2SO_4 is added to remove HCl. 5 drops of dil.HNO_3 & 50mg of $NaBiO_3$ are added and shaken. Purple colour of $HMnO_4$ indicates **Manganese.**	solution is boiled, 3 drops of dil.HCl is added and cooled. 2 drops of 2% aq. soln. of tannin and aq. NH_3 are added. Deep blue colour . To another portion, 3 drops of aq.NH_3 is added and H_2S is passed. Red colour indicates **Vanadium**			

1. Residue: Cerium oxalate. 3 drops of 2N NaOH are added and boiled. Centrifuged and the residue is dissolved in dil.HNO_3.
   3 drops of dil. aq. NH_3 and 2 drops of 6% H_2O_2 are added to 2 drops of the solution and heated. Yellowish brown CeO_2 indicates
   Cerium.
   A drop of conc. HNO_3 is added to the 2 drops of the solution and boiled. It is evaporated to dryness and the residue is extracted with three drops of water and one drop of 5% alcoholic solution of anthranilic acid. Dark blue ppt is formed which rapidly dissolves to a brown solution. This indicates **Cerium**.

2. Centrifugate: Oxalato complex of thorium. 5 drops of dil HCl are added to the solution. White ppt of $Th(C_2O_4)_2$ is formed.
   5 drops of 2N NaOH are added, boiled and centrifuged. So formed, residue $Th(OH)_4$ is dissolved in dil.HCl. Just neutralized with aq.NH_3 and 5 droops of m-nitroibenzoic acid reagent is added. Heated to 80^0C. White ppt indicates **Thorium**.

Thenard"s blue test: Al^{+3} is best confirmed by the Thenard's blue test since Be^{+2} interferes in the aluminon and alizarins tests. The residue of $Al(OH)_3$ is shaken with a little water and poured on a piece of filter paper. Two drops of $Co(NO_3)_2$ solution are then added and the paper is burnt. Blue tinted ash (Thenard's blue) shows aluminium.

Quinalizarin test for Be^{+2}: Quinalizarin (1:2:5:8 – tetrahydroxy anthraquinone gives a blue colour with Be^{+2} in faintly alkaline medium. The reagent is 0.05% solutionj in 0.1N NaOH. Al^{+3}, Mg^{+2} ions interfere in this test. Al^{+3} gives a red-violet colour while Mg^{+2} gives a similar blue colour. In alkaline solutions Al^{+3} does not interfere if present in small quantities. The interference from Mg^{+2} is overcome by adding as drop of bromine water.

Analysis of Group IV

To the centrifugate from III group cations, aq. NH_3 is added if necessary and H_2S is passed till the completion precipitation. Heated for a few minutes and centrifuged. The residue washed with 1 c.c. water and washings are added to centrifugate.

<table>
<tr><td colspan="4"><i>Residue:</i> Stirred with 1 c.c. water and 5 drops of dil. HCl are added and centrifuged.</td></tr>
<tr><td colspan="2"><i>Residue:</i> CoS and NiS. 5 to 10 drops of conc. HCl is added and transferred to a beaker. A small crystal of $KClO_3$ is added, boiled and evaporated jut to dryness. Dissolved in 1 c.c. water and divided into two portions.</td><td colspan="2"><i>Centrifugate</i>: Zn^{2+}, Mn^{2+}.
NaOH is added in slight excess and centrifuged.</td></tr>
<tr><td>To 5 drops of solution, a few crystals of NH_4CNS and 10 drops of amyl alcohol are added and shaken. Blue alcohol layer shows
Cobalt.</td><td>To 5 drops of solution, 3 drops of dimethylglyoxime reagent and aq. NH_3 are added. Scarlet ppt indicates
Nickel</td><td><i>Residue</i>: $Mn(OH)_2$
It turns brown in air. 10ml of dil. HNO_3 and about 50mg $NaBiO_3$ are added. Stirred well and centrifuged. Pink coloured centrifugate shows
Manganese</td><td><i>Centrifugate</i>:
Divided into two portions.
(i) H_2S is passed through a pool of the solution. White or dry white ppt
(ii) A part of the solution is acidified with HOAc and $[K_4Fe(CN)_6]$ is added.
White ppt indicates
Zinc</td></tr>
</table>

Analysis of group V

The centrifugate from zinc group is neutralized with dil.HNO_3 and evaporated to dryness. Heated continuously to remove ammonia salts by volatalisation and cooled. The ppt is dissolved in the minimum quantity of dil. HCl and 3 drops in excess are added. Neutralised with aq.NH_3 and 2 drops are added in excess. Saturated $(NH_4)_2CO_3$ solution is added dropwise to precipitate cations completely. The precipitate is digested and centrifuged. Washed with 1 c.c. water and washings are added to the centrifugate.

<u>Residue</u>: Dissolved in the minimum amount of dil HOAc, then 3 drops of K_2CrO_4 solution are added and centrifuged.		*<u>Centrifugate</u>*: Examined for group VI cations.
<u>Residue</u>: Yellow $BaCrO_4$ Dissolved in conc.HCl and examined flame colour. Transient green colour indicates **Barium**	*<u>Centrifugate</u>*: Ca^{+2}, Sr^{+2} Neutralised with aq.NH_3. Reprecipitated as carbonates, centrifuged and the centrifugate is rejected. Residue is redissolved in dil HOAc and tested as described below: (i) <u>Test for Sr^{+2}</u>: To 3 drops of solution, 3 drops of $CaSO_4$ solution is added, boiled and let to stand. White ppt of $SrSO_4$ is formed. Centrifuged and the centrifugate is discorded, stirred with 5 drops of water and poured on a small piece of filter paper. The paper is charred, moisted the product with conc. HCl, the flame colour is examined. Flashes of crimson indicates **Strontium** (ii) <u>Test for Ca^{+2}</u>: To 5 drops of the solution, 5 drops of saturated $(NH_4)_2SO_4$ solution is added, boiled, cooled and centrifuged. (a) To one half of the centrifugate, 3 drops of 3% ammonium oxalate solution followed by aq.NH_3 are added. Formation of white ppt indicates Ca^{2+}. It is confirmed by flame test to give brick red colour. (b) To other half of centrifugate, 3 drops of saturated NH_4Cl and 3 drops of $[K_4Fe(CN)_6]$ are added and allowed to stand. Pale yellow ppt indicates **Calcium**	

ANALYSIS OF GROUP VI

This group includes Mg^{+2} , NH_4^+ and the alkali metals (Li^+, Na^+ and K^+). NH_4^+ is tested out in the beginning of cation analysis itself.

Evaporate the centrifugate from group V to dryness, add 5 drops of conc. HNO_3 and evaporate cautiously till there are no more fumes. Extract residue with water. Divide into several portions,

Test for Mg^{2+}:

a) To 3 drops of the solution 2 drops of NH_4Cl, 2 drops of aqueous ammonia and three drops of Na_2HPO_4 are added. The sides of the tube are scratched with a glass rod. White crystalline precipitate of $MgNH_4PO_4$ shows magnesium.

b) To 3 drops of the test solution 5 drops dil. HCl are added. Stirred and one drop of magneson reagent and then NaOH solution is added drop wise. Blue precipitate confirms Mg.

Magneson reagent: 10 mg of magneson (p-nitrobenzoresorcinol) is dissolved in 100 ml of 1 N NaOH solution.

Test for Na^+:

a) To 5 drops of the solution an equal quantity of-zinc uranyl acetate and 10 drops of ethanol are added. Shaken and allowed to stand. Yellow crystalline precipitate shows sodium.

b) To 5 drops of the solution, 5 drops of uranyl magnesium acetate solution and a few drops of methanol are added. Yellow crystalline precipitate of sodium magnesium acetate confirms sodium.

c) A few drops of the solution are mixed with 2 drops of conc. HCl and performed flame test. Golden yellow colour shows sodium.

Test for K^+:

a) To 3 drops of the solution, 3 drops sodium hexanitritocobaltate (III) [cobalt nitrite] solution and then 6 drops of ethanol are added. Shaken and allowed to stand. Yellow precipitate shows potassium.

b) To 3 drops of the solution, 3 drops of a freshly prepared saturated solution of tartaric acid are added. To it 5 drops alcohol and are added and shaken vigorously. White precipitate show potassium.

c) A few drops of the solution are mixed with 2 drops of conc. HCl and performed flame test. Pale violet (lilac) colour shows potassium.

Test for Li^+:

a) To 5 drops of the solution, a few drops of ammonium hydroxide are added till ammonical and NH_4F solution is added. Slow formation of a white gelatinous precipitate indicates lithium.

b) To 5 drops of the solution, an equal quantity of zinc uranyl acetate and 10 drops of methanol are added. Shaken and allowed to stand. Like in sodium test, yellow crystalline precipitate forms. The precipitate is $LiZn[(UO_2)_3(Oac)_9].6H_2O$.

c) To 3 drops of the solution, 2 drops of conc.HCl are added. Flame test is done. Scarlet red colour indicates lithium.

Test for Cs^+:

Cesium imparts a blue colour to the flame and Cs^+ forms a bright red precipitate with $KBiI_4$.

Feric periodate reagent: **Dissolve 2g KIO_4 in 10cc of freshly prepared 2 N KOH solution. Dilute to 50cc with water add 3 cc of 10% $FeCl_3$ solution and dilute to 100cc with 2N KOH.**

Prof. K. Rambabu

M.Sc. CHEMISTRY (Previous), DEGREE EXAMINATION
SECOND SEMESTER
PRACTICAL - I: PHYSICAL CHEMISTRY MANUAL (R22CH25)

(For the students admitted from the A.Y. 2025-2026 onwards)

1) Potentiometric determination of Fe(II) with Cr(VI)
2) pH-metric determination of strong acid with strong base.
3) Conductometric titration of strong acid with strong base
4) Verification of Beers Law using potassium permanganate.

EXPERIMENT -1

Potentiometric determination of Fe(II) with Cr(VI)

Aim:

To determine the strength and amount of the ferrous salt present in the given solution potentiometrically.

Apparatus and Chemicals Required:

Potentiometer, calomel electrode, platinum electrode, potassium dichromate (N/10) and solution of ferrous salt (~N/10). 2N sulphuric acid etc.

1) *0.1N Ferrous Ammonium sulphate solution*:

About 9.8035 g of Ferrous Ammonium Sulphate is weighed accurately transfer the substance through funnel dissolve in small amount of 2N H_2SO_4 and made up to the mark with 2N Sulphuric acid.

2) 0.*1N Potassium dichromate solution*:

About 1.225 g of potassium dichromate is weighed accurately, transfer the substance through the funnel and made up to the mark with distilled water.

Principle:

When dichromate solution is added to a solution containing ferrous ions, the ferrous ions get oxidized to ferric ions and a platinum electrode is dipped in the solution to pick up redox potential developed. The potential raised in system containing species of oxidised and reduced state is given by.

$$E_{red} = E^{0}_{red} - RT/nF * \ln a_{red}/a_{ox}$$

The Potential developed depends on the activities of the species (or concentrations of the species taking the activity coefficient as unity in dilute solutions) and it may be combined with another half cell (calomel electrode) to determine the change of activities on adding the oxidizing agent. After the oxidation of all ferrous ions into ferric ions, the redox system will be Cr_2O_7/Cr which has a different redox potential. This forms the basis of potentiometric titrations redox systems.

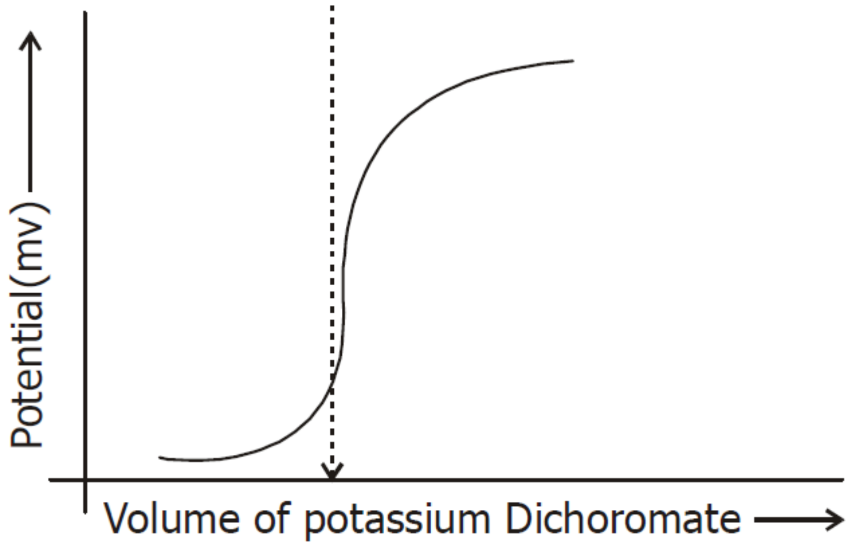
Procedure:

The given Ferrous salt solution in 100 mL volumetric flask is made up to the mark with 2N sulphuric acid. Pipette out 20 mL of the ferrous salt solution into a 100 mL beaker. Add equal quantity of dilute sulphuric acid and dip a bright platinum electrode a calomel electrode into the solution. Titrate the solution in the beaker against potassium dichromate taken in the burette noting down the emf after each addition. In the beginning 1 mL or 0.5 mL addition. The end point is reflected by a sudden change in emf. Take some more readings after the end point. Plot the value of emf against the volume of dichromate added. From the titre value calculate the strength of ferrous salt solution and hence the amount of it present in the given solution.

Calculations:

Pilot Titration				Accurate Titration		
S.No	Vol. of $K_2Cr_2O_7$ (mL)	Potential (mv)		S.No	Vol. of $K_2Cr_2O_7$ (mL)	Potential (mv)

Graph Representation:



From graph volume of Potassium Dichromate [V_1] = _____mL

Normality of Potassium Dichromate [N_1] = 0.1 N

Volume of Ferrous Ammonium Sulphate [V_2] = 10 mL

Normality of Ferrous Ammonium Sulphate [N_2] = _____mL

We know that

$$V_1N_1 = V_2N_2$$

Therefore, $N_2 = \frac{N1V1}{V2}$

Amount of Ferrous Ammonium Sulphate present in the given 100 mL of solution

$$= \frac{N_2 \text{ X } 392.14 \text{ X } 100}{10000} =$$

* [Gram molecular weight of Ferrous Ammonium Sulphate = 392.14]

[Note: Space for calculation]

Report:

Amount of ferrous Ammonium sulphate present in the given 100 mL of solution = ———

EXPERIMENT - 2

pH-metric determination of strong acid with strong base.

Aim:

Perform pH metric titration of a strong acid (Hydrochloric acid) with a strong alkali, (Sodium hydroxide). Take 25 mL of 0.05 M HCl in 50 mL beaker and titrate with 0.1M NaOH solution in an interval of 0.5 mL.

Apparatus Required:

A pH meter (an electronic meter and glass combination electrode), 50 mL beaker, burette and burette stand, wash bottle, pipette, plastic funnel, glass rod.

Chemicals Required

0.05 M HCl solution, 0.1 M NaOH solution, Distilled water.

Theory:

Most of the chemical and biochemical processes are profoundly affected by the acidity or alkalinity of the medium in which the reaction takes place. All acids dissociate in aqueous solution to yield H^+ ions. Some acids like HCl, H_2SO_4, HNO_3 etc. are completely ionized in aqueous medium where as CH_3COOH, HCOOH etc. ionize to a small extent only. The former are known as strong and the later as weak acids. pH of any solution is defined as ($-\log H^+$) and has values between 0–14. $pH < 7$ indicate acidic solution, $pH > 7$ indicate basic solution and $pH = 7$ means neutral solution.

In an acid-base titration, the important information to obtain is the equivalence point. It is the point at which an equal amount of acid has been neutralised by equal amount of base or vice versa. If there are a number of moles of acid in the titration flask, the equivalence point is reached when that same number of moles of base added is the same as the number of moles acid in the titration flask, and the volume of the base added is also known. Similarly, if the number of moles acid in the titration flask is unknown, it can be calculated for the equivalence point if the molarity of the base and the volume of base added are known.

The pH of a solution can be measured accurately with the help of a pH meter. Measurement of pH is employed to monitor the cause of acid-base titration. It affords a direct method of obtaining a titration curve. The titration curve is a graph of measured pH values versus the volume (mL) of titrant added. The pH values of the solution at different stage of acid–base neutralization are determined and plotted against the volume of alkali added on adding a base to an acid, the pH rises slowly in the initial stages as the concentration of H^+ ion decreases gradually due to the consumption of some amount of HCl by NaOH resulting in the formation of NaCl (whose amount will be the same as that of NaOH added).

$$HCl\ (aq) + NaOH\ (aq) \rightarrow NaCl\ (s) + H_2O\ (l)$$

But, at the equivalence point (the point at which an equal amount of acid has been neutralised by equal amount of base or vice versa), pH increases rapidly as at the equivalent point H^+ ion concentration is very small. Then it flattens out after the end point. The end point of the titration can be detected where the pH value changes most rapidly. However, the shape of the curve depends upon the ionizability of the acid and the base used and also on the acidity of base and basicity of the acid.

Once a titration curve is constructed and the equivalence point established the experimenter could then chose an indicator to perform the titration calorimetrically that would give a suitable endpoint (point at which indicator changes colour).

Indicator:

The pH at the equivalence point is 7 and slightly before and after the equivalence point, it encompasses an interval from pH = 3 to pH = 11. Therefore, any indicator whose pH range is within this interval i.e. indicators which will change their colour within this pH range can be used. *However, the range of the steep change of pH at the equivalence point depends upon the concentrations of acid and base being titrated.* Methyl orange, methyl red and phenolphthalein, the common laboratory indicators can be used for this purpose as their respective pH ranges lie in the interval 3-11. The usual choice, however, is phenolphthalein because the colour change in this case is from colourless to a slight pink colour, a change which can be easily detected.

Procedure:

1. 0.1(M) NaOH solution is provided.

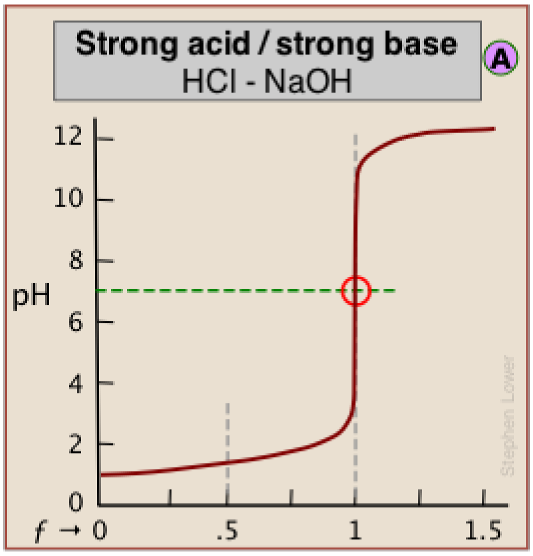
2. HCl solution of unknown strength is provided.

3. Calibrate the pH meter with the solutions of pH 4,7 and 10.

4. pH-metric Titration: Clean the electrode with distilled water and wipe them with tissue paper or filter paper. Take 25 mL of HCl solution in a 50 mL beaker and immerse the electrode in it. Note down the pH range. Rinse the burette with distilled water and then with NaOH solution. After that fill the burette with NaOH solution. The reading shown on the scale of pH meter is pH value of the HCl solution. Add NaOH solution drop wise from the burette (maximum 0.5 mL at a time), shake the solution well with the help of glass rod and note the corresponding pH values. Near the end point, volume of NaOH added should be as small as possible (0.1 ml at a time, which is the least count of a burette that we use in our laboratory) because the acid is neutralized and there will a sharp increase in pH values.

Further addition of even 0.01 mL of NaOH, increase the pH value to about 9-10. Put back the selector to zero position after each pH measurement, and always keep the selector at zero position when it is not in use.

Plot the graph were seen below figure for pH of solution *verses* volume of NaOH added.



Observations and Calculations

1. Preparation of 250 mL 0.05 M standard oxalic acid solution

Mass, w of oxalic acid to be weighed for the preparation of Solution

$$W = \frac{0.05 \times 126 \times 250}{1000} = 1.5750 \text{ g}$$

2. Titration of standard oxalic acid solution against NaOH

Solution in burette = NaOH

Solution in titrating flask = V_1= 20 mL standard oxalic acid

Indicator used = Phenolphthalein

End point = colourless to pink

S.No	**Volume of Oxalic acid (V_1 mL)**	**Burette Readings**		**Volume of NaOH solution (V_2 mL)**
		Initial (mL)	**Final (mL)**	
1				
2				
3				
4				
5				

Molarity of given NaOH solution (M_2):

$$M_2 = \frac{M1V1}{n1} = \frac{M2V2}{n2}$$

(Standard oxalic acid) (NaOH)

$n_1 = 1$; $n_2 = 2$

$$M_2 = \frac{M1\ x\ V1\ x\ n2}{V2\ x\ n1}$$

Molarity of given NaOH solution (M_2) = ______ M.

Table 1: pH metric Titration

Volume of HCl taken (V_3) (mL)	**Volume of NaOH Added (V_4) (mL)**	**pH**
25 mL		

Table 2: Volume of HCl corresponding pH and calculated data

S.No	**V_{NaOH}**	**pH**	**$\Delta pH = pH_f - pH_i$**	**$\Delta V = V_f - V_i$**	**$\Delta pH / \Delta V$**	**$V_{avg} = (V_i + V_f)/2$**

Molarity of given HCl solution:

$$\frac{M3V3}{1} = \frac{M2V4}{1}$$

(Given HCl) (NaOH)

$$M_3 = \frac{M2 \ x \ V2}{V3}$$

Strength of the given HCl will therefore be = $S_1 = M_3$ x 126 =

Plot a graph between pH and volume of NaOH (V_{NaOH}) added. There should be a region in your graph where the slope is very steep. Determine the mid-point of this region. This is the equivalence point. Find out the corresponding volume of NaOH required (V_4 mL) for complete neutralization of HCl from the graph. Then find out the strength of HCl (S_1).

$$25 \text{ x } M_3 = V_4 \text{ x } M_2$$

(HCl) (NaOH)

Strength of HCl (S_1) = (M_1) x 126 (molar mass of HCl)

Plot a graph between $\Delta pH/\Delta V$ and V_{avg}. There should be a peak in your graph which is the equivalence point. Find out the corresponding average volume of NaOH required (V_4 mL) for complete neutralization of HCl from the graph. Then find out the strength of HCl (S1).

Result

The strength of the unknown HCl (S_1) = ________ g/L^{-1}

Precautions

(i) Electrodes must be immersed in the solution properly and sufficient time to be allowed for the electrodes to obtain the temperature of the solution.

(ii) pH meter should be calibrated before the experiment.

(iii) Magnetic stirrer may be used or the solution be stirred mechanically from time to time during pH metric titration using glass rod.

(iv) Leave the selector in zero position when it is not in use.

(v) The glass electrode should always be kept dipping in the distilled water when not in use.

EXPERIMENT - 3

Conductometric titration of strong acid with strong base

Aim:

To determine the strength of the given HCl Solution Conductometrically.

Chemicals Required:

1. NaOH Solution
2. HCl
3. Oxalic acid.
4. Phenolphthalein.

Preparation of Standard Oxalic Acid Solution (0.1N):

About 3.15 g of Oxalic acid di hydrate is weighed accurately and dissolved in small amount of distilled water and made up to the mark in a 250 mL Volumetric flask.

Preparation of 0.1N Sodium Hydroxide:

About 1 g of Sodium Hydroxide is dissolved in small amount of water and diluted to 250 mL and standardized against standard Oxalic acid Solution.

Theory:

The conductivity of HCl solution is very high due to mobility of H^+ ions in it. When a solution of strong alkali is added to the solution of Strong acid, the highly conducting H_3O^+ ions are replaced by Na^+ ions is considerably Smaller than H_3O^+ and hence addition of alkali to the acid is always accompanied by a decrease in conductivity. When all the H_3O^+ ions are replaced, i.e.; after the endpoint, further addition of NaOH results in increase in conductivity.

From the plot of the Conductance *vs* Volume of NaOH added, the end point can be calculated.

Procedure:

Standardization of Sodium Hydroxide Solution:

20 mL of Oxalic acid is pipetted out in to a Conical flask and is diluted to 30 mL with distilled water. To the solution, two drops of Phenolphthalein indicator is added and then titrated against Sodium Hydroxide taken in a burette. The end point is colourless to pale pink. The experiment is repeated till concurrent readings are obtained.

Determination of Strength of given HCl Solution: The given unknown HCl solution in 100 mL Volumetric flask is made upto the mark and then 10 mL of the given Unknown HCl Solution is taken in a 100 mL beaker. To this 40 mL of distilled water is added. The electrode of the cell is dipped in the solution. The conductivity of the solution is noted before adding the alkali. The standardized Sodium Hydroxide is added from a Burette with 1 ml of increment and by shaking thoroughly, the Contents of the beaker the conductivity values are noted. The values of observed conductivities are plotted ordinate against volume of Sodium Hydroxide added as abscissa.

The concentration of Hydrochloric acid is determined using the end point from the graph.

Precautions:

After each addition of the titrant from the burette, the solution should be thoroughly stirred and then the reading should be taken.

Report:

The strength of the Hydro Chloric acid is _______ gms / Litre.

Calculations:

1) 0.1 N Oxalic Acid

$$N = \frac{\text{Amount of Oxalic Acid}}{63.035} \times \frac{1000}{250}$$

= ________ N

Standardization of Sodium Hydroxide Solution:

S.No	Volume of Oxalic acid (V_1 mL)	Burette Readings		Volume of NaOH solution (V_2 mL)
		Initial (mL)	Final (mL)	
1				
2				
3				
4				
5				

We know that $V_1N_1 = V_2N_2$

Where Volume of Oxalic acid Solution [V_1] = 20.0 mL
Normality of Oxalic acid Solution [N_1] = _____N
Volume of Sodium Hydroxide solution [V_2] = ______mL
Normality of Sodium Hydroxide solution [N_2] = _____N

Therefore,

$$N_2 = \frac{N1V1}{V2}$$

[Note: Space for calculation]

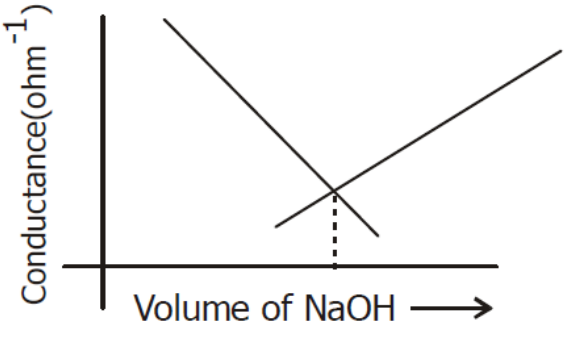
Normality of Sodium Hydroxide [N_2] = ...N

Determination of Strength of Hydro Chloric Acid:

V_3 = Volume of Hydrochloric acid = 10.0 mL

S.No.	Vol.of HCl	Conductivity (Ohm^{-1})

Graph Representation



Where Volume of Sodium Hydroxide solution from graph [V_2] = ____ ml
Normality of Sodium Hydroxide solution [N_2] = _____N
Volume of Hydrochloric acid solution [V_3] = 10.0 ml
Normality of Hydrochloric acid in the mixture [N_3] = _____N

$$V_2N_2 = V_3N_3$$

Therefore

$$N_3 = \frac{N2V2}{V3}$$

[Note: Space for calculation]

Strength of HCl acid = Normality of HCl acid in solution X Eq.Wt. of HCl

= N_3 X 36.5 = _______________ gm/Liter.

REPORT:

Amount of HCl present in the given solution = _______ gm/Liter.

EXPERIMENT - 4

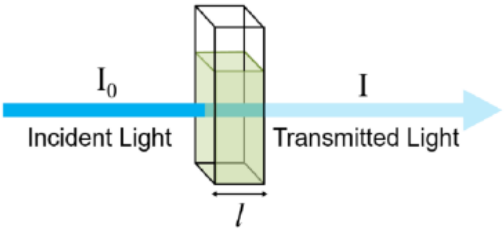
Verification of Beers Law using Potassium Permanganate.

Aim:

To verify Lambert-Beer's law using a given solution of potassium permanganate at the wavelength of its maximum absorption (λ_{max}) and consequent determination of the unknown concentration of a solution of potassium permanganate.

Theory:

The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length (cuvette length), UV/Vis spectroscopy can be used to determine the concentration of the absorber in a solution. The absorbance changes with concentration. Thus, a higher concentration of the coloured solution absorbs more light (and transmits less) than a solution of lower concentration.



$$\log(I_o/I_t) = A = \varepsilon c l$$

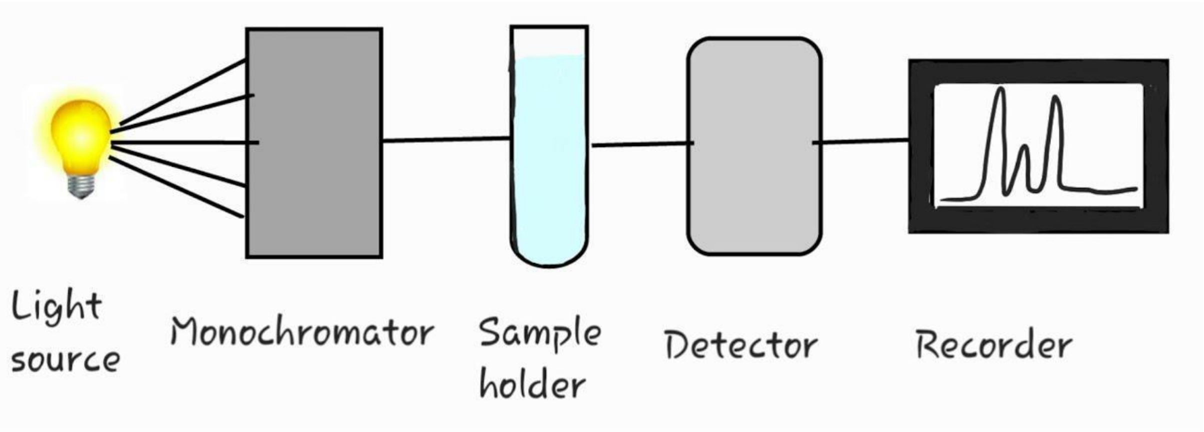
According to Beer–Lambert law,

$\log(I_o/I_t) = A = \varepsilon cl$ where I_o and It are the incident and transmitted intensities,

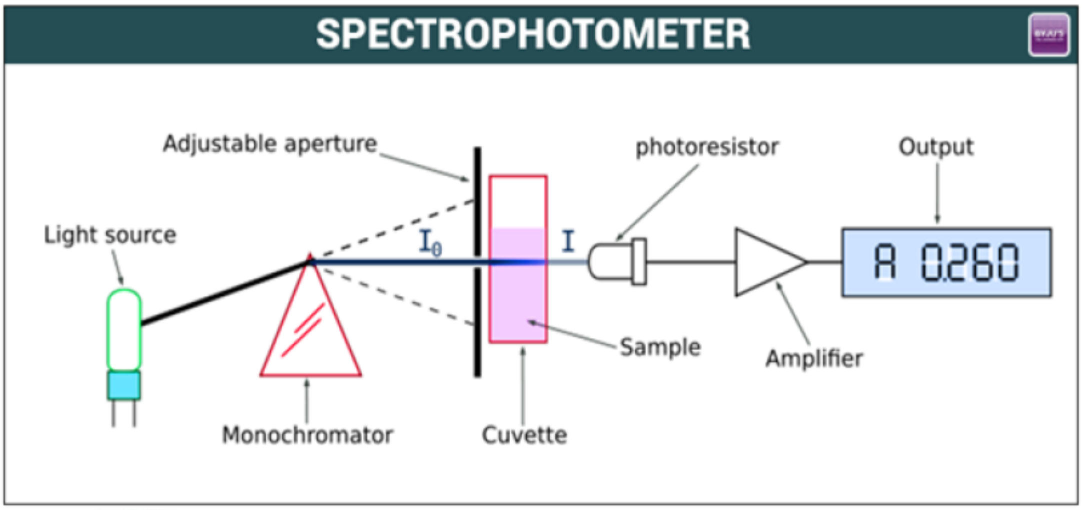
A = absorbance and ε is a constant i.e. absorptivity (also called the extinction coefficient).

If the concentration is measured in mol/L^{-1}, the absorptivity is called molar absorptivity.

$A = \varepsilon cl$. At constant length $A \propto c$.



Working principle of spectrophotometer



Spectrophotometer **Cuvette**

Requirements:
Spectrophotometer, Cuvette, six test tubes, Measuring cylinder, 10 mL pipette, 0.001 M $KMnO_4$ solution, distilled water, test tube rack, and tissues (preferably lint-free).

Procedure & observation table:

Step 1: To record the absorbance of $KMnO_4$ solution at different wavelengths to determine the light wavelength for its maximum absorption (λ_{max}):

(a) Prepare 100 mL of 0.001M $KMnO_4$ (Molecular weight 158.03 gm/mol) solution in distilled water.
(b) Label five clean, dry, test tubes 1–5.
(c) Use a 10 mL pipette to prepare five standard solutions according to **Table 1**.
(d) Thoroughly mix each solution.
(e) Calibrate the spectrophotometer with respect to the blank solution i.e. distilled water.
(f) Fill any one of the prepared solutions (1-5) up to a certain level in the cuvette of the spectrophotometer.
(g) Record the absorbance of the respective solution at different wavelengths as mentioned in

Table 2.

(h) Plot the absorbance data in the graph paper with respect to the wavelength and calculate the ight wavelength for its maximum absorption (λ_{max}) in $KMnO_4$.

Table 1:

Test-tube	0.001M $KMnO_4$ (mL)	Distilled water (mL)	Concentration (M)
1	1	9	
2	2	8	
3	3	7	
4	4	6	
5	5	5	

Table 2:

The solution of the ……… No. test tube was chosen for the determination of the light wavelength for its maximum absorption (λ_{max}).

Entry	Wavelength (λ in nm)	Absorbance
1		
2		
3		
4		
5		

Step 2: To record the absorbance of different concentrations of solutions at the specified λ_{max}:

(a) Set the operating wavelength of the spectrophotometer in the range of absorption maxima of aqueous $KMnO_4$ solution (λ_{max}).

(b) Calibrate the spectrophotometer with respect to the blank solution i.e. water.

(c) Fill each of the solutions up to a certain level in the cuvette of the spectrophotometer.

(d) Record the absorbance of the respective solutions as stated in **Table 3**.

(e) Plot the absorbance data in the graph paper with respect to the concentration which should be a straight line passing through the origin.

Table 3:

Entry	Test-tube	Absorbance
1		
2		
3		
4		
5		

Step 3: Determination of the unknown concentration of a given potassium permanganate solution:

(a) Fill the solutions up to a certain level in the cuvette of the spectrophotometer.

(b) Record the absorbance of the given solution of unknown concentration.

(c) Plot the absorbance data in the same graph obtained above (ideally it should be on the same straight line obtained from the plot of step 1)

(d) Draw a perpendicular line from the absorbance point to the concentration axis.

(e) Note down the corresponding unknown concentration.

Conclusion:

1) The light wavelength for its maximum absorption (λ_{max}) is found to be ………… nm.

2) The concentration of the unknown solution was found to be ………….. M.

Precautions:

(a) Always mix the standard solutions properly.

(b) Wipe the outside of the cuvette every time with a lint-free tissue.

(b) Handle cuvettes only by the top edge of the ribbed sides.

(c) Dislodge any bubbles by gently tapping the cuvette on a hard surface.

(d) Always position the cuvette so the light passes through the clear sides.

(e) Always set the light source of the instrument in the absorption maxima range of the given solution.

Molecular Weights and Equivalent Weights of Some Substances

S.No.	Chemical name	Molecular weight (M.wt)	Equivalent weight (Eq.wt)
1	Hydrochloric acid (HCl)	36.5	36.5
2	Sulphuric acid (H_2SO_4)	98	49
3	Sodium Carbonate (Na_2CO_3)	106	53
4	Sodium hydroxide ($NaOH$)	40	40
5	Oxalic acid ($H_2C_2O_4.2H_2O$)	126	63
6	Hypo ($Na_2S_2O_3.5H_2O$)	248.19	248.19
7	Potassium permanganate ($KMnO_4$)	158	31.6
8	Potassium dichromate ($K_2Cr_2O_7$)	249318	49.03
9	Copper sulphate ($CuSO_4.5H_2O$)	249.6	249.6
10	Ferrous Ammonium Sulphate $(NH_4)_2$ $FeSO_4.5H_2O$	392.14	392.14
11	Potassium Iodide (KI)	166	166
12	Sodium chloride ($NaCl$)	58.44	58.44

Concentrated Acids

Acids	Specific gravity	%By-Weight	Approximate Normally
Hydrochloric acid	1.19	37.9	12N
Nitric Acid	1.42	69.8	16N
Sulphuric acid	1.84	96.0	36N
Acetic acid (glacial)	1.05	99.5	17N
Phosphoric acid	1.71	86.0	15N

Prof. R. Ramesh Raju