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KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Established Under Section 3 of UGC Act 1956)

COIMBATORE-21

Syllabus-II B.Sc Chemistry

Semester-IV

16CHU412 ORGANOMETALLIC CHEMISTRY PRACTICAL 4H 2C

Instruction Hours/week:L:0 T:0 P:4 Marks: Internal: 40 External: 60 Total:100

Scope

The lab course deals with the Qualitative semimicro analysis of mixtures containing cations and anions along with an interfering anion, spot tests and Principles involved in chromatographic separations.

Objectives

This lab course enables the student to

1. Understand how to identify the anions and the cations in a mixture by Qualitative semimicro analysis
2. Understand to identify the interfering anion
3. Understand the principles behind the spot tests
4. Understand the principles of chromatographic separations

Methodology

Qualitative semimicro analysis

Qualitative semimicro analysis of mixtures containing 3 anions and 3 cations. Emphasis should be given to the understanding of the chemistry of different reactions. The following radicals are suggested:

CO_3^{2-}, NO^{2-}, S^{2-}, SO_3^{2-},$S_2O_3^{2-}$, CH_3COO^-, F^-,Cl^-, Br^-, I^-, NO^{3-}, BO_3^{3-}, $C_2O_4^{2-}$, PO_4^{3-}, NH^{4+}, K^+, Pb^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, Sn^{2+}, Sb^{3+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}

Mixtures should preferably contain one interfering anion, **or** insoluble component ($BaSO_4$, $SrSO_4$, $PbSO_4$, CaF_2 or Al_2O_3) **or** combination of anions e.g. $CO_3^{2-}$and SO_3^{2-}, NO_2-and NO_3^-, Cl-and Br-Cl-and I-, Br-and I, $NO_3^-$and Br^-, $NO_3^-$and I^-

Spot tests should be done whenever possible.

Principles involved in chromatographic separations. Paper chromatographic separation of following metal ions:

i. Ni (II) and Co (II)

ii. Cu(II) and Cd(II)

Suggested Reading

1. Svehla, G. (2006) Vogel's *Qualitative Inorganic Analysis*, Longman, New York.

INORGANIC ANALYSIS

Aim

To analyze the given inorganic mixture systematically.

Apparatus required

Test tubes, centrifuge tubes, baeker, glass rod, watch glass, test tube holder, china dish, spatula, dropper.

Chemicals required

Sodium hydroxide, dil.HCl, H_2S, hydrazine hydrochloride, NH4OH, (NH4)2CO3 acetic acid, potassium iodide, oxalic acid, hydroxylamine hydrochloride, ammonium acetate.

SEMI-MICRO QUALITATIVE ANALYSIS

ANALYSIS OF AN INORGANIC MIXTURE

S.No	Experiment	Observation	Inference
1	Colour and appearance	(i)White coloured solid (ii)Green coloured solid	(i)Absence of Cu &Ni (ii)May be presence of Cu & Ni
		(iii) Blue coloured solid	(iii) May be Cu
		(iv) Black coloured solid	(iv)May be presence of Co & Ni
		(v) Yello coloured solid	(v) Absence of Co & Ni
2	Solubility test: A small amount of the mixture is dissolved in dil.HCl	(i)Soluble in dil.HCl	(i)May be absence of I group metals
		(ii)Insoluble in dil.HCl	(i)Presence of I group metals
3	Flame test: To a small amount of the mixture conc. HCl is added to make a paste and is introduced into a non-luminous flame with a burnt end of the match stick	(i)Crimson-red coloured flame	(i)Strontium
		(ii)Lilac coloured flame	(ii)Lithium
		(iii)Bluish green coloured flame	(iii)Copper
		(iv) Green coloured flame	(iv) Barium & Thallium
		(v) Brick red coloured flame	(v) Calcium
4	Test for ammonium: A small amount of the mixture is heated with NaOH	Ammonia gas evolves on heating	Presence of ammonia

PREPARATION OF ORIGINAL SALT SOLUTION

Prepare the original salt solution by dissolving the mixture either in

(i) Dil.HCl either in hot or cold condition (or)
(ii) Dil.HNO_3 either in hot or cold condition (or)
(iii) Conc.HCl either in hot or cold condition (or)
(iv) Conc.HNO_3 either in hot or cold condition (or) aquaregia

SEPARATION OF CATIONS INTO GROUPS

To a portion of the original salt solution, **dil.HCl** is added and centrifuged.

<table>
<tr><td rowspan="8">Residue: Presence of I group metals</td><td colspan="8">Centrifugate : A few crystals of hydrazine hydrochloride are added, heated and centrifuged.</td></tr>
<tr><td rowspan="7">Residue: Presence of IA group metals</td><td colspan="7">Centrifugate :dil. HCl is added , H_2S is passed and centrifuged.</td></tr>
<tr><td rowspan="6">Residue: Presence of II group metals</td><td colspan="6">Centrifugate :H_2S boiled off, and NH_4Cl , NH_4OH in excess are added and centrifuged.</td></tr>
<tr><td rowspan="5">Residue: Presence of III group metals</td><td colspan="5">Centrifugate :NH_4Cl , NH_4OH are added and H_2S is passed ,the solution is centriguged.</td></tr>
<tr><td rowspan="4">Residue: Presence of IV group metals</td><td colspan="4">Centrifugate :H_2S gas is boiled ,NH_4Cl, NH_4OH and $(NH_4)_2CO_3$ are added then centrifuged.</td></tr>
<tr><td rowspan="3">Residue: Presence of V group metals</td><td colspan="3">Centrifugate : The centrifugate is evaporated to dryness. A few drops of conc.HNO_3 are added again evaporated. The residue is extracted with water and divided into several portions.</td></tr>
<tr><td>To the first portion NH_4Cl,NH_4OH and Na_2HPO_4 are added .the sides of the test tube are scralated with glass rod. White crystalline precipitate. Presence of magnesium.</td><td>To the second portion picric acid is added. yellow precipitate. Presence of pottasium.</td><td>To the third portion equal amounts of zinc uranyl acetate and a few drops of ethanol are added. The solution is shaken well and allowed to stand. Yellow precipitate. Presence</td><td>To the fourth portion NH_4OH , NH_4Cl and NH_4F are added. Gelatinous white precipitate. Presence of lithium.</td><td>To the last portion Nessler, s reagent and NaOH are added. Reddish brown precipitate. Presence of ammonium.</td></tr>
</table>

								of **sodium.**		

ANALYSIS OF I-GROUP METALS

To the I group residue 3ml of water is added, boiled and centrifuged.

<table>
<tr><td colspan="3">Residue: A few drops of aq.NH_3 is added and centrifuged.</td><td colspan="2">Centrifugate:A few drops of conc.H_2SO_4 are added , boiled and 1 ml of water is added, centrifuged.</td></tr>
<tr><td rowspan="2">Residue:A 3drops of conc. HCl, 1drops of conc.HNO_3 are added , boiled and centrifuged.
To the centrifugate 3drops of stannous chloride are added. White precipitate turning grey shows the presence of mercury.</td><td colspan="2">Centrifugate: Dil.HCl is added in drops till a precipitate is formed.KI is added and centrifuged.</td><td rowspan="2">Residue(White)
5 drops of NH_4Ac are added and warmed. 2 drops acetic acid and 2 drops of K_2CrO_4 are added. Yellow precipitate shows the presence of lead.</td><td rowspan="2">Centrifugate:
Centrifugate is neutalised with dil.NH3 and 2 drops KI and sodium thio sulphate are added. Yellow precipitate shows the presence of Thallium. Thallium is confirmed by flame test (Green flame)</td></tr>
<tr><td>Residue(Yellow)
Insoluble in NH_4OH. Presence of silver.</td><td>Centrifugate:The solution is centrifuged. Two drops of stannous chloride, conc. HCl are added and warmed. Blue precipitate shows the presence of tungsten.</td></tr>
</table>

ANALYSIS OF I A-GROUP METALS

<table>
<tr><td colspan="4">To the I group residue two drops of conc.HCl and two drops of bromine water are added. The solution is boiled and saturated ammonium chloride are added and centrifuged.</td></tr>
<tr><td rowspan="4">Residue: Orange yellow. Presence of platinum.</td><td colspan="3">Centrifugate: A few crystals of oxalic acid are boiled and centrifuged.</td></tr>
<tr><td rowspan="3">Residue: Brown precipitate. Presence of Gold.</td><td colspan="2">Centrifugate: Aq.NH_3 in excess is added and then dil.HCl is added and centrifuged.</td></tr>
<tr><td rowspan="2">Residue: Yellow crystals. Presence of Palladium.</td><td colspan="2">Centrifugate: A small quantity of hydroxylamine hydrochloride is added ,warmed and centrifuged.</td></tr>
<tr><td>Residue: Red precipitate. Presence of Selenium.</td><td>Centrifugate: A few crystals of hydrazine hydrochloride is added and boiled. Blue black crystalline precipitate. Presence of Tellurium.</td></tr>
</table>

ANALYSIS OF II A AND II B-GROUP METALS

To the second group precipitate **1ml of NaOH** is added, boiled and centrifuged.

Residue: Presence of II A group precipitate.	**Centrifugate : Dil.HCl** is added, boiled and centrifuged. The precipitate is warmed with water and analyzed for II B group.

ANALYSIS OF II A-GROUP METALS

II A group precipitate is washed with water. To the residue 1.5ml of dil.HNO_3 are added and boiled. Two drops of dil.H_2SO_4 are added and centrifuged.

Residue: Residue is washed with water and centrifuged. NH_4OAc is added, boiled are centrifuged.		**Centrifugate:NH_4OH** is added in excess boiled and centrifuged.	
Residue:3 drops of conc.HCl and 3 drops of conc.HNO_3 are added. The solution is heated and diluted with water. 2 drops of stannous chloride are added. **Grayish white precipitate.** Presence of **Mercury**.	**Centrifugate:**1 drop of acetic acid and 2 drops of K_2CrO_4 are added. **Yellow precipitate**. Presence of **Lead.**	**Residue:**The residue is dissolved dil.HCl and 3 drops of stannite solution are added. **Black and white** precipitate. Presence of **Bismuth.**	**Centrifugate:** Centrifugate is divided into two portions. 1. To one portion acetic acid and $K_4Fe(CN)_6$.Reddish **brown precipitate** confirms the presence of **copper.** **2.** To the second portion add conc. HCl and excess water are added H_2S gas is passed**. Yellow precipitate** confirms the presence of **Cadium.**

ANALYSIS OF II B-GROUP METALS

To the II B group precipitate NH_4Cl and few drops of con.HCl are added and stirred well, boiled, diluted with water centrifuged.

<table>
<tr><td colspan="2">Residue: 5 drops of ammonium carbonate is added stirred well and centrifuged.</td><td rowspan="2">Centrifugate: Centrifugate is divided into two portions
1. To the first portion Zn dust is added, boiled and the metal is dissolved. 3 drops of $HgCl_2$ are added. White or grey precipitate shows the presence of Tin
2. To the second portion oxalic acid crystals are added and diluted with water. H_2S is passed. Orange precipitate shows the presence of antimony.</td></tr>
<tr><td>Residue: (Dark brown)
3 drops of con HCl and 2 drops of bromine water are added. Excess of bromine is expelled by boiling. The solution is diluted. 10% NH_4CNS, 3 drops of $SnCl_2$ and 10 drops of amyl alcohol are added and shaken well.
Red alcohol layer shows the presence of Molybdenum.</td><td>Centrifugate: Centrifugate is acidified with dil.HCl. Yellow precipitate shows the presence of arsenic.</td></tr>
</table>

ANALYSIS OF III-GROUP METALS

To the III group precipitate minimum amount of dil.HCl is added and Oxalic acid crystals are added. The precipitate is digested in hot water and centrifuged.

<table>
<tr><td colspan="2">Residue: 1ml of $(NH_4)_2C_2O_4$ is added and centrifuged.</td><td colspan="5">Centrifugate: Centrifugate is neutralized with aq.NH_3. Digested and centrifuged. The residue is washed with NH_4Cl . 1ml of H_2O and 50mg of Na_2O_2 are heated. The solution is boiled till the effervescence ceases and centrifuged.</td></tr>
<tr><td>Residue: 3 drops of NaOH are added, boiled and centrifuged. The residue is dissolved in dil.HNO_3 and divided into 2 portions
1.To 0ne portion NH_4OH, 6% H_2O_2 are added and boiled. Yellowish brown precipitate shows the presence of cerium.
2. To the second portion 2 drops of con.HNO_3 are added, boiled and evaporated to dryness. The residue is extracted with water and few drops of 5% alcoholic solution of anthranlic acid are added. Dark blue precipitate rapidly dissolves to brown solution. Shows the presence of Cerium.</td><td>Centrifugate: 5 drops of dil.HCl are added. To the white precipitate formed 5 drops of NaOH are added, boiled and centrifuged. The residue is dissolved in dil.HCl and neutralized with NH_4OH. 5 drops of m-nitro benzoic acid are added and heated to boil. White precipitate shows the presence of Thorium.</td><td colspan="2">Residue: Residue is dissolved in dil.HCl ,boiled and divided into 3 portions.
1.To one portion 2 drops of KI and $Na_2S_2O_3$ are added yellow precipitate shows the presence of Thallium.
2.To the second portion H_3PO_4 is added to decolorize iron. 2 drops of 6% H_2O_2 & 2 drops of dil.H_2SO_4 are added. White precipitate shows zirconium. Orange colour solution shows titanium. Centrifuge the solution.
<table><tr><td>Residue: White precipitate shows Zirconium.</td><td>Centrifugate:20 mg of Na_2SO_3 are added & boiled. White precipitate shows Titanium.</td></tr></table>3.To third portion a drop of con.H_2SO_4 and concentrate are added .5 drops of HNO_3&50mg of $NaBiO_3$ are added.The solution is stirred and allowed to stand.purple colour of $KMnO_4$ shows presence of aMnganese.
.</td><td colspan="3">Centrifugate: 5 drops of $Pb(NO_3)_2$ and 200mg of NH_4OAc crystals are added. The solution is acidified with HNO_3 is stirred well and centrifuged.
<table><tr><td>Residue: The residueis dissolved in 10 drops of dil HNO_3 boil & cooled. Amyl alcohol and 6%H_2O_2 are added. The solution is shaken well.
(i)Blue alcohol layer shows Chromium.
(ii)Reddish brown aqueous layer is divided into 2 parts.
1.To one part 3 drops of dil.HCL are added boil & cooled.2 drops of 2% aq.solution of Tannin & NH_4OH are added. Deep blue colour shows the presence of Vanadium.
2.To the second part NH_4OH is added H_2S gas is passed.Red colour shows Vanadium.</td><td>Centrifugate: 3 drops HCL,H_2S is passed and centrifuged. The Pbs is precipitated. The centrifugate is boiled ,cooled and $(NH_4)_2CO_3$ solution is added. The solution is boiled and centrifuged.
<table><tr><td colspan="2">Residue: Residue is dissolved in dil.HCl &2 drops of $Na_2S_2O_3$are added boiled and centrifuged.</td><td rowspan="2">Centrifugate: Centrifugate is concentrated and dil. HCl, $K_4Fe(CN_6)$ and aq.NH_3 are added. Brown precipitate turns yellow on adding NaOH. Presence of Uranium.</td></tr><tr><td>Residue: Residue is shaken well with H_2O & few drops of $Co(NO_3)_2$.A burnt piece of filter paper is dipped in the above solution. Blue tinted ash (Thenard`s blue) shows the presence of Aluminium.</td><td>Centrifugate: Centrifugate is added with Quninalizarin. Blue colour shows the presence of Beryllium.</td></tr></table></td></tr></table></td></tr>
</table>

ANALYSIS OF GROUP –IV (MAGNESIUM AND LITHIUM)

To centrifugate from group v is evaporated to dryness. 5 drops of conc. HNO_3 and evaporated cautiously. The solution is ignited till there no fumes. The residue is extracted with water. The solution is divided into several portions.

1. **Magnesium**
   (a) To 3 drops of solution, 2 drops of NH_4Cl, 2 drops of aq. NH_4 and 3 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 of dil.HCl are added. Add one drop of magneson reagent and then drops of NaOH are added. Blue precipitate confirms Magnesium.
2. **Lithium**
   (a) Lithium imparts a scarlet-red colour to the flame.
   (b) A gelatinuous precipitate slowly on addition of NH_4F to an ammonical solution.
   (c) A white precipitate is formed when ferric periodate reagent is added to a Li^+ solution.
   (d) A yellow precipitate is formed with zinc uranyl acetate reagent.

ANALYSIS OF V GROUP METALS

V group residue is dissolved in minimum amount of dil.acetic acid. A few drops K_2CrO_4 solution are added and centrifuged.

<table>
<tr><td rowspan="3">Residue: (Yellow) residue is dissolved in con.HCl and introduced into a non-luminous flame with a burnt end of match stick. Green coloured flame shows presence of Barium.</td><td colspan="3">Centrifugate: Centrifugate is neutralized with NH_4OH. The solution is reprecipitated with $(NH_4)_2CO_3$ & centrifuged. The residue is redissolved in dil.acetic acid and divided into two portions.</td></tr>
<tr><td rowspan="2">To the first portion $CaSO_4$ is added, boiled ane centrifuged. The residue stirred few ccs of H_2O. A piece of charged of filter paper is dipped in the above solution. The product is moistened con.HCl and introduced into a non luminous flame with the burnt end of the match stick. Crimson red-coloured flame shows presence of Strontium.</td><td colspan="2">To the second portion add $(NH_4)_2SO_4$ boil, cool and centrifuge. Divide into two portions.</td></tr>
<tr><td>To the first portion ammonium oxalate and aq.NH_3. White precipitate shows presence of Calcium.</td><td>To the second portion NH_4Cl and potassium ferro cyanide are added. Pale yellow precipitate shows presence of Calcium.</td></tr>
</table>

ANALYSIS OF IV GROUP METALS

To the IV group precipitate 5 drops of HCl is added, shaken well and centrifuged.

<table>
<tr><td rowspan="2">Residue: Residue is dissolved in aquaregia and evaporate to dryness.The residue con.HCl added and divide into two portions.
1. To the first portion, NH_4CNS (or acetic acid and potassium ferricyanide) and amyl alcohol are added and shaken well. Blue alocohol layer shows the presence of Cobalt.
2. To the second portion, DMG is added and excess of NH_4OH is also added. Scarlet precipitate shows the presence of Nickel.</td><td colspan="2">Centrifugate: Boil off H_2S and then add NaOH in excess and centrifuged.</td></tr>
<tr><td>Residue:

(Turns brown in air) Dil.HNO_3 50mg of $NaBiO_3$ are added and stirred and centrifuged. Pink colour solution shows the presence of Manganese.</td><td>Centrifugate: Divide into two portions
1. To the first portion H_2S gas is passed Dirty white precipitate. Presence of Zinc.
2. To the second portion acetic acid and $K_4[Fe(CN_6)]$ are added. White precipitate shows the presence of Zinc.</td></tr>
</table>

Analysis of group –VI (Magnesium and Lithium)

The centrifugate from group v is evaporated to dryness. 5 drops of conc. HNO_3 added and evaporated cautiously. The solution is ignited till there no fumes. The residue is extracted with water. The solution is divided into several portions.

3. **Magnesium**
   (c) To 3 drops of solution, 2 drops of NH_4Cl, 2 drops of aq. NH_4 and 3 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.
   (d) To 3 drops of the test solution, 5 drops of dil.HCl added. Add one drop of magneson reagent and then drops of NaOH are added. Blue precipitate confirms Magnesium.
4. **Lithium**
   (e) Lithium imparts a scarlet-red colour to the flame.
   (f) A gelatinuous precipitate slowly on addition of NH_4F to an ammonical solution.
   (g) A white precipitate is formed when ferric periodate reagent is added to a Li^+ solution.
   (h) A yellow precipitate is formed with zinc uranyl acetate reagent.

ANALYSIS OF V GROUP METALS

V group residue is dissolved in minimum amount of dil.acetic acid. A few drops K_2CrO_4 solution are added and centrifuged.

<table>
<tr><td rowspan="3">Residue: (Yellow) residue is dissolved in con.HCl and introduced into a non-luminous flame with a burnt end of match stick. Green coloured flame shows presence of Barium.</td><td colspan="3">Centrifugate: Centrifugate is neutralized with NH_4OH. The solution is reprecipitated with $(NH_4)_2CO_3$ & centrifuged. The residue is redissolved in dil.acetic acid and divided into two portions.</td></tr>
<tr><td rowspan="2">To the first portion $CaSO_4$ is added, boiled ane centrifuged. The residue stirred few ccs of H_2O. A piece of charged of filter paper is dipped in the above solution. The product is moistened con.HCl and introduced into a non luminous flame with the burnt end of the match stick. Crimson red-coloured flame shows presence of Strontium.</td><td colspan="2">To the second portion add $(NH_4)_2SO_4$ boil, cool and centrifuge. Divide into two portions.</td></tr>
<tr><td>To the first portion ammonium oxalate and aq.NH_3. White precipitate shows presence of Calcium.</td><td>To the second portion NH_4Cl and potassium ferro cyanide are added. Pale yellow precipitate shows presence of Calcium.</td></tr>
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ANALYSIS OF IV GROUP METALS

To the IV group precipitate 5 drops of HCl is added, shaken well and centrifuged.

<table>
<tr>
<td rowspan="2">Residue: Residue is dissolved in aquaregia and evaporate to dryness.The residue con.HCl added and divide into two portions.
3. To the first portion, NH_4CNS (or acetic acid and potassium ferricyanide) and amyl alcohol are added and shaken well. Blue alocohol layer shows the presence of Cobalt.
4. To the second portion, DMG is added and excess of NH_4OH is also added. Scarlet precipitate shows the presence of Nickel.</td>
<td colspan="2">Centrifugate: Boil off H_2S and then add NaOH in excess and centrifuged.</td>
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<td>Residue:

(Turns brown in air) Dil.HNO_3 50mg of $NaBiO_3$ are added and stirred and centrifuged. Pink colour solution shows the presence of Manganese.</td>
<td>Centrifugate: Divide into two portions
3. To the first portion H_2S gas is passed Dirty white precipitate. Presence of Zinc.
4. To the second portion acetic acid and $K_4[Fe(CN_6)]$ are added. White precipitate shows the presence of Zinc.</td>
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