17CHU412 ORGANOMETALLIC CHEMISTRY- PRACTICAL 4H 2C

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

Course Objectives

This lab course enables the student to

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

Course Outcome

This lab course enables the student to understand and

1. Can identify the anions and the cations in a mixture by Qualitative semimicro analysis.
2. Can identify the interfering anion.
3. Can identify the radicals by doing spot tests.
4. Able to do chromatographic separations.

Experiments

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_2or 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:

Text Books:

1. Svehla, G. (1996). *Vogel's Qualitative Inorganic Analysis* (VII Edition). Longman, New York.
2. Venkateswaran, R., Veeraswamy, R. & Kulandaivelu, A.R. (2015). *Basic Principles of Practical Chemistry*. S. Chand & Sons Ltd., New Delhi.
3. Thomas A.O. (2003). *Practical Chemistry for B.Sc Main Students*. Scientific Book Centre, Cannore, Kerala.

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University)
(Established Under Section 3 of UGC Act 1956)
Coimbatore - 641 021.
(For the candidates admitted from 2017 onwards)

DEPARTMENT OF CHEMISTRY

SUBJECT NAME: Organometallic Chemistry Practical

SUBJECT CODE: 17CHU412

SEMESTER: IV **CLASS: II B.Sc CHEMISTRY**

LECTURE PLAN
DEPARTMENT OF CHEMISTRY

S.No	Lecture Hour	Topics to be Covered	Support Materials/ Page Nos
		UNIT I	
1.	4	Demonstration and writing experimental procedures	
2.	4	Identification of simple salt	T1:5-70
3.	4	Identification of mixture of salts-I	T1:5-70
4.	4	Identification of mixture of salts-II	T1:5-70
5.	4	Identification of mixture of salts-III	T1:5-70
6.	4	Identification of mixture of salts-IV	T1:5-70
7.	4	Identification of mixture of salts-V	T1:5-70
8.	4	Paper Chromatography separation Cu(II) and Ni(II)	
9.	4	Viva-voce examination	
10.	4	Modal Examination practical	
Total No of Hours Planned = 40			

SUPPORTING MATERIALS:

Suggested Readings:

Text Book:

T1: Venkateswaran, V., Veerasamy. R. & Kulandaivelu, A. R. (2015). *Basic Principles of Practical Chemistry*, Sultan Chand & Sons

INORGANIC QUALITATIVE ANALYSIS

EXPERIMENT	OBSERVATION	INFERENCE
1. Colour and appearance	1. Blue or green 2. Pink 3. Green 4. Colourless solid	Presence of copper Presence of cobalt, manganese Presence of manganese Absence of copper, manganese and cobalt
2. Solubility a) In water b) In dil. HCl	 Soluble Insoluble Soluble Insoluble	 May be ammonium salts Absence of ammonium salts Absence of lead May be due to lead
3. Flame colour test: A pinch of given substance is made into paste with 2 or 3 drops of conc. HCl in a watch glass. The paste is taken at the end of a charred splinter and introduced into the edge of non-luminous flame. The colour of the flame is noted.	1. Bright green 2. Bluish green 3. Light Yellowish green 4. Brick red 5. No characteristic coloured flame	Presence of borate Presence of copper Presence of barium Presence of calcium Absence of borate, copper, barium and calcium
4. The flame test is performed with the substance and conc. H_2SO_4.	A bright green colour is imparted No bright green coloured flame	Presence of borate Absence of borate
5. Boron trifluoride test:		

A pinch of the substance is mixed with calcium fluoride and a drop of conc.H_2SO_4 is added and made into a paste. It is taken at the end of charred splinter and introduced into the edge of non-luminous flame.	A bright green colour is imparted to the flame. No bright green colour is imparted to the flame.	Presence of borate Absence of borate
6. <u>Ethyl Borate test</u>: A pinch of substance is mixed with 2cc of ethyl alcohol and 10 drops of conc.H_2SO_4 in a test tube. It is heated and the vapour is ignited.	The vapour burns with a green edged flame. The vapour does not burn with green edged flame.	Borate confirmed. Borate is absent.
7. <u>Action of heat:</u> A small portion of the substance is heated in a dry test tube.	1. Colourless gas turning lime water milky. 2. Colourless gas with smell of NH_3 and fuming with conc. HCl is evolved. 3. Red brown gas turning ferrous sulphate paper brown. 4. White sublimate is formed. 5. Yellow when hot white when cold.	Presence of carbonate and oxalate Presence of ammonium salts Presence of nitrate Presence of ammonium salts Presence of zinc

	6. No characteristic change.	Absence of carbonate, oxalate, ammonium, nitrate and zinc
8. **Action of sodium hydroxide**: A pinch of substance is boiled with 5 cc of NaOH solution.	Colourless pungent smelling gas is evolved. It turns red litmus blue and gives dense white fumes with glass rod dipped in conc. HCl. No characteristic gas	Presence of ammonium Absence of ammonium
9. Action of dil. HCl: A pinch of the substance is treated with 3 cc of dil. HCl in a test tube.	1. Brisk effervescence of colourless gas is evolved. It turns lime water milky. 2. Colourless gas with the smell of rotten egg turning lead acetate paper black. 3. No characteristic change	Carbonate is confirmed. Sulphide is confirmed. Absence of carbonate and sulphide.
10. Action of dil. H_2SO_4 and MnO_2: To a pinch of the substance, a pinch of MnO_2 and 3 cc of dil. H_2SO_4 are added and warmed gently	Effervescence takes place and colourless gas is evolved turning lime water milky. No Effervescence takes place	Presence of oxalate Absence of oxalate
11. Action of Conc. H_2SO_4: A pinch of the substance is heated	1. Colourless gas giving	Presence of chloride

with 2 cc of conc. H_2SO_4	dense white fumes with ammonia is evolved. 2. Colourless gas giving white precipitate with a glass rod dipped in water. Oily appearance at the top of the test tube. 3. Yellowish brown vapour evolves on continued boiling and no action of fluorescence paper. 4. A colourless gas evolves turning lime water milky. 5. No characteristic gas is evolved	 Presence of fluoride Presence of nitrate Presence of oxalate Absence of chloride, fluoride, nitrate and oxalate
12. <u>Test for halides</u>: A pinch of the substance is mixed with a pinch of MnO_2 and 2 cc of conc. H_2SO_4 and warmed gently	1. Colourless gas evolves which turns lime water milky. 2. Greenish yellow gas evolves which turns starch iodide paper blue. 3. Red brown gas has no action with fluorescence paper. 4. No characteristic change	Presence of oxalate Presence of chloride Presence of nitrate Absence of oxalate, chloride and nitrate

13. <u>Chromyl chloride test:</u> A pinch of the substance is warmed with a few amount of potassium dichromate and conc. H_2SO_4.	Red brown gas is evolved forming yellow precipitate with lead acetate solution. No red brown gas	Presence of chloride Absence of chloride.
14. <u>Test for nitrate:</u> A pinch of substance is heated with 2 c c of conc. H_2SO_4 and pieces of copper turning are added and warmed.	Red brown gas turning ferrous sulphate paper brown. No red brown gas is seen.	Presence of nitrate. Absence of nitrate.
15. <u>Ammonium molybdate test:</u> A pinch of the substance is dissolved in few drops of conc. HNO_3 and the clear solution is heated with 5-10 cc of ammonium molybdate solution, shaken well and heated gently	A bright yellow precipitate at once or gradually in the cold. No yellow precipitate	Presence of phosphate. Absence of phosphate.
16. <u>Action of conc. HCl and tin:</u> A little of the substance is heated with a pinch of tin metal and a few drops of conc. HCl.	Colourless rotten egg smell gas turning lead acetate paper black No rotten egg smell	Presence of sulphide Absence of sulphide

Preparation of sodium carbonate extract:

A little of the given substance is mixed with three times of sodium carbonate and one test tube of distilled water in a boiling tube and the contents are boiled for ten minutes. The solution is filtered and the filtrate is used for the following reactions.

1. <u>Barium Chloride Test:</u> To about 1 cc of the extract, dil. HCl is added drop by drop till the effervescence stops. The contents are heated, cooled and barium chloride solution is added.	A white precipitate insoluble in conc. HCl is formed. No white precipitate is formed.	Sulphate is confirmed. Absence of sulphate.
2. <u>Silver Nitrate Test:</u> To about 1 cc of the extract, dil. HNO_3 is added drop by drop till the effervescence stops. The contents are heated, cooled and Silver nitrate solution is added. If no precipitate on adding $AgNO_3$, then few drops of ammonium hydroxide are added drop by drop.	A curdy white precipitate soluble in ammonium hydroxide is formed. No curdy precipitate is formed. A yellow precipitate is obtained in the form of a ring. No characteristic ring is seen	Chloride is confirmed. Absence of chloride. Presence of phosphate Absence of phosphate
3. About 1 cc of the extract is boiled with few drops of conc. HNO_3 and cooled. Then it is shaken with 10 cc of ammonium molybdate	A yellow precipitate is formed on cold or on gentle warming	Presence of phosphate

solution.	No yellow precipitate precipitate	Absence of phosphate
4. Calcium chloride Test: About 2 cc of the extract is acidified with acetic acid, boiled with 5 cc of calcium chloride solution.	A white precipitate is obtained	Presence of fluoride or oxalate.
If there is a white precipitate obtained in the above experiment, it is filtered off. The white precipitate is dissolved in 3 cc of dil. H_2SO_4, heated and to the clear solution, a dil. solution of $KMnO_4$ is added drop by drop.	1. $KMnO_4$ solution is decolourised. 2. $KMnO_4$ solution is not decolourised.	Oxalate is confirmed. Fluoride is confirmed
5. Brown Ring Test: About 2 cc of the extract is acidified with dil. H_2SO_4 and the mixed with 3 cc of strong ferrous sulphate solution. Conc. H_2SO_4 is added along the sides of the tube.	A brown ring is formed at the junction of the two liquids. No brown ring is formed.	Nitrate is confirmed. Absence of nitrate.

Removal of Interfering radicals:

1. Elimination of borate and fluoride:

A portion of the given substance is mixed with 5 cc of conc. HCl in a boiling tube. The mixture is evaporated to a paste and cooled. 5 cc of conc. HCl is added and again evaporated to a paste. The process is repeated four times. The paste is finally mixed with 10 cc of water. If any precipitate is formed, it is used for the analysis of I group cations. The solution is used for the analysis from II group.

2. Elimination of oxalate:

A portion of the given substance is roasted strongly in a china dish for 20 minutes. The mass is then cooled and mixed with 10 cc of conc. HCl. The mixture is boiled and filtered. The filtrate is evaporated to a paste. The paste is finally mixed with 10 cc of water. If any precipitate is formed, it is used for the analysis of I group cations. The solution is used for the analysis from II group.

3. Elimination of phosphate:

The phosphate radical is eliminated before proceeding to group III. A few drops of the filtrate from group II, after the removal of H_2S. To the neutral solution, zirconyl chloride ($ZrOCl_2$) is added and the precipitate got is removed. The process is repeated till no precipitate is obtained.

ANALYSIS OF BASIC RADICALS

Separation of cations into groups

A small amount of the substance is dissolved in water, dil. HCl or conc. HCl (The residue should examined for I group)

To 1 cc of the original solution, dil.HCl is added and centrifuged.

<table>
<tr><td rowspan="4">Residue: White

Presence of I group</td><td colspan="3">Centrifugate: To the filtrate H_2S gas is passed and centrifuged.</td></tr>
<tr><td rowspan="3">Characteristic Residue:

Presence of II group</td><td colspan="2">Centrifugate: It is boiled to expel H_2S and then added 2 drops of conc. HNO_3 and boiled with ammonium chloride and excess of ammonium hydroxide and centrifuged</td></tr>
<tr><td rowspan="2">Characteristic Residue:

Presence of III group</td><td colspan="2">Centrifugate: H_2S is passed and centrifuged</td></tr>
<tr><td>Characteristic Residue:

Presence of IV group</td><td>Centrifugate: Boiled to expel H_2S. Boiled with dil. HNO_3, concentrated to reduce the volume. Then ammonium chloride, ammonium hydroxide and ammonium carbonate are added and centrifuged.</td></tr>
</table>

				Residue: White Presence of V group	**Centrifugate:** Analysed for VI group

DETECTION OF CATIONS: ANALYSIS OF I-GROUP

The white residue is washed, boiled with water and centrifuged while hot.

<table>
<tr><td colspan="2">Residue: Shaken with ammonium hydroxide and centrifuged</td><td rowspan="2">Centrifugate:
i) To one part, KI solution and water are added. A small amount of the yellow precipitate is dissolved by heating and cooled. Golden spangles appear. Lead is confirmed.
ii) To the second part, potassium chromate is added. Yellow precipitate. Lead is confirmed.</td></tr>
<tr><td>Residue: Black. 3 drops of conc. HCl and 1 drop of conc, HNO_3 are added and centrifuged. To the clear Centrifugate, stannous chloride is added. White silky precipitate turning grey. Hg^{2+} is confirmed.</td><td>Centrifugate:
Dil. HNO_3 is added. White precipitate. Ag^{+} is confirmed.</td></tr>
</table>

ANALYSIS OF II A GROUP

The residue is washed with 1 cc of water, 1 cc of dil. HNO_3 and 1 cc dil H_2SO_4 are added boiled and centrifuged.

<table>
<tr><td rowspan="2">No residue
Absence of mercury and lead.</td><td colspan="2">Centrifugate: Ammonium hydroxide is added in drops to excess, boiled and centrifuged.</td></tr>
<tr><td>Residue: It is dissolved in dil. HCl and poured into excess water.</td><td>Centrifugate: Divided into two portions.
1. To one portion, a few drops of acetic acid is added and followed by potassium ferrocyanide.</td></tr>
</table>

	White turbidity. Presence of bismuth.	Red brown precipitate. Copper is confirmed. 2. To another portion, a small amount of water and H_2S gas is passed. Yellow precipitate is formed. Cadmium is confirmed.

ANALYSIS OF III GROUP

The residue is washed with water, boiled with water and centrifuged.

Residue: Brown	**Centrifugate:** Dil. HCl, 1 g of solid ammonium chloride are added. Gelatinous white precipitate. Aluminium is confirmed.
1. One part is dissolved in dil. HCl and the solution is divided into two parts. a) To one part potassium ferricyanide is added. Prussian blue precipitate. Ferric ion is confirmed. b) To another part potassium thiocyanate is added. Blood red colour. Ferric ion is confirmed. 2. The second part of the precipitate is boiled with conc. HNO_3 & a pinch of lead oxide or sodium bismuthate is added, diluted and allowed to stand. Pink colour of permanganate is obtained. Manganese is confirmed.	

ANALYSIS OF IV GROUP

The residue is washed with water and stirred with dil. HCl and centrifuged.

Residue: Black. It is boiled with	**Centrifugate:** Boiled to expel H2S and slight excess NaOH is added and centrifuged.

conc.HCl & a crystal of potassium chlorate and evaporated to dryness. Blue residue – cobalt; yellow residue – nickel. It is dissolved in water. 1. To one part, ammonium thiocyanate and amyl alcohol are added and shaken well-alcohol layer is blue. Cobalt is confirmed. 2. To another part, ammonium chloride, ammonium hydraoxide and dimethyl glyoxime are added. A rosy red precipitate - nickel is confirmed.	**Residue:** 1. One part is boiled with PbO_2 and conc. HNO_3 and diluted. Pink colour – Manganese is confirmed. 2. Another part is fused with KOH and $KClO_3$, green residue turns pink. On adding dil. H_2SO_4 confirms manganese.	**Centrifugate:** 1. Through one part, H_2S is passed. White precipitate- zinc is confirmed. 2. To another part, acetic acid and potassium ferricyanide are added. White precipitate- zinc is confirmed. 3. The precipitate in (1) is dissolved in conc. HNO_3, 2 drops of cobalt nitrate is added. A filter paper dipped in the solution is burnt to ash. Green ash-Zinc is confirmed.

ANALYSIS OF V GROUP

The residue is washed with water and dissolved in minimum amount of acetic acid, potassium chromate is added and centrifuged.

Yellow Residue: Barium is confirmed. Dissolved in conc. HCl. Flame colour test is performed. Green coloured flame-barium is confirmed.	**Centrifugate:** 1. To this, ammonium chloride, ammonium hydroxide and ammonium oxalate solutions are added. White precipitate – Calcium is confirmed. 2. Flame colour test is performed with the precipitate. Brick red coloured flame. Calcium is confirmed.

ANALYSIS OF VI GROUP

Centrifugate from V group is concentrated to a small volume by evaporation and divided into two portions.

1. To one part, ammonium chloride, ammonium hydroxide and disodium hydrogen phosphate are added. The inner side of the test tube is scratched with a glass rod. White crystalline precipitate. Magnesium is confirmed.
2. To the second part, sodium hydroxide is added in excess. White precipitate insoluble in excess of NaOH confirms magnesium.

Test for ammonium radical:

1. Heat a little mixture with 2-3 cc of NaOH in a test tube. A characteristic smell of ammonia is obtained. On bringing a glass rod dipped in conc. HCl on the mouth of the test tube, enormous white fumes are produced, ammonium is confirmed.
2. On adding Nessler's reagent to the solution of the mixture – Brown colour or precipitate. Ammonium is confirmed.

Report:

The given inorganic mixture contains

Acid Radicals: 1)

2)

3)

Basic Radicals: 1)

2)

3)