LABORATORY EXPERIMENT **B.Sc. Semester: 7** **PRACTICAL MANUAL**

COURSE: (PMJDSC - Major) **(GROUP- A & GROUP- B)**

COURSE CODE:SC23PMJDSCCHE701

GROUP –A

1. **INORGANIC QUALITATIVE ANALYSIS HAVING SIX REDICALS** (MINIMUM EIGHT)
(OUT OF SIX ONE MUST BE FROM RARE GROUP AND ONE MUST BE TRACE IN A MIXTURE)

NEGATIVE REDICALS : Cl^-,Br^-,I^-,CO_3^{-2},NO_3^{-1},$N0_2^{-1}$,PO_4^{-3},BO_3^{-3},CrO_4^{-2}

POSSITIVE REDICALS : FROM 1^{ST} AND 2^{ND} GROUP AND V^{TH}-B

RARE : FROM 1^{ST} AND 2^{ND} GROUP AND V^{TH}-B

TRACE : Br^-,I^-,CO_3^{-2},NO_3^{-1},$N0_2^{-1}$.

Preliminary Test	Observation	Inference (Possible Ions)
Colour of Mixture	White	Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Zn^{2+} salts
	Blue	Cu^{2+}
	Yellow	Chromate (CrO_4^{2-}), Cd^{2+} salts
Solubility in Water	Completely soluble	May contain Na^+, K^+, NH_4^+, NO_3^-, Cl^-, CH_3COO^- salts
	Partially soluble	Mixture may contain both soluble and insoluble salts
	Insoluble	May contain $BaSO_4$, $PbSO_4$, AgCl, $CaCO_3$, $SrSO_4$, metal oxides or sulphides

Dry Test

No.	Dry Test	Observation	Inference
1	Flame test	1. Green-blue flame	Cu^{+2} OR BO_3^{-3}
		2. Pale violate	K^{+1}
		3. Golden yellow	Na^{+1}
		4. Crimson red	Li^{+1}
2	Sodium hydroxide test Mix+NaOH	1. Ammoniacal Smell	NH_4^{+1}
		2. Yellow precipitate of mercury(II) oxide	Hg^{+1}
3	Mixture + dil. HCL (Heat mix. Slowly)	1. Break effervesces of CO2	CO_3^{-2}
		2. After heating Yellow- red color gas evolved	NO_2^{-1}
		3. Add DW -White ppts	Pb^{+1} (1^{st} group may be Present)
4	Mixture + ¼ amount of MnO2 + Con. H_2SO_4 (Heat mix. Slowly)	1. Violet colur gas evolved	CO_3^{-2}
		2. Reddish-brown vapours are evolved which tern starch paper yellow	Br^-
		3. Reddish-brown vapours are evolved which tern starch paper yellow which don't turns starch paper yellow	NO_3^{-1}
		4. Greenish-yellow gas evolved gives white fumes with Ammoniacal solution	Cl^-
4	Mixture + Con. HCl (Heat mix. Slowly)+ Con. HNO_3 (excess amout)+ Ammonium Molibledom	1. Yellow ppt,s	PO_4^{-3}
5	In silica dish Mixture + Con. H_2SO_4 (Mix well) add some amount of Ethanol, Heat Mixture and fire it.	Green flame	BO_3^{-3}
6	Water extract (W.E.) + Zinc Urenileacetate	White Ppt,s	Na^+
7	Water extract (W.E.) + Picric acid	Yellow ppt"s	K^+

8	Water extract (W.E.) [Yellow coloured + dil. HCL + Pass H2S	Yellow to Orenge colour terns Green colour	CrO_4^{-2}
9	Soda extract + dil. H2SO4 + small amount of Zn dust + heat mix add +KI (s) + Starch Solution	Blue Colour solution	NO_3^{-1} Presence (Br^-)

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Wet Test for Positive Radical

Preparation of the Original solution:

Take small quantity of the Mixture and examine the solubility in the following solvents in the order given:

1. **Water (Cold and hot)**
2. **Dil. HCl (Cold and hot)**
3. **Conc. HCl (Cold and hot)**
4. **Dil. HNO_3 (Cold and hot)**
5. **Conc. NHO_3 (Cold and hot)**
6. **Aqua Regia (3 parts of Conc. HCl + 1 part of Conc. HNO_3 , mix and use the solution immediately, do not keep it at all)**

Group Separation for Positive Radical

Original Solution (O.S.)+Add Dilute HCl **Precipitate → Group I (Ag+, Pb2+, Hg+) & (Tl; W)**

▼

Filtrate + Add H2S (g) in Dilute HCl (Acidic Medium) **Precipitate → Group II (Cu2+, Cd2+, Bi3+, As3+, Sb3+, Sn2+) & (Se;Te;Mo)**

▼

Filtrate used for test of **(Na+, K+, NH4+) and Li+**

Group Classification-1

The **Group I (Silver Group)** residue is washed using 2 cm^3 of dilute HCl (see instruction 9) and then with 2 cm^3 of water. Discard the washings. Boil residue in the centrifuge tube with 2 cm^3 of water and centrifuge while hot. Decant the centrifugate into a test tube. Repeat extraction with 2 cm^3 boiling water and combine the centrifugate.

Residue: White – Hg_2Cl_2 or AgCl. Yellow - H_2WO_4.
Boil the residue with 5 cm^3 of dilute NH_3 solution and centrifuge.

Centrifugate: May contain Pb^{2+}or Tl^+, which may crystallize on cooling. Carefully add 1 cm^3 of conc. H_2SO_4 and evaporate till fumes are seen. Cool and dilute carefully to 5 cm^3 with water. If a precipitate is formed, centrifuge.

Residue: Black precipitate, consisting of a mixture of $Hg(NH_2)Cl$ and Hg.

Dissolve the residue by heating with 2 cm^3 of aqua regia, cool and do the following tests:

1) To 1 cm^3 of the solution, add NaOH solution in drops with shaking till excess. A black precipitate of Hg_2O is formed.

2) To 1 cm^3 of the solution, add K_2CrO_4 solution and heat. A brown precipitate changing to red Hg_2CrO_4 on heating.

3) Spot test: Place a drop of faintly acid test solution (original) on a drop reaction paper and add a drop of saturated potassium nitrite (KNO_2) solution. A black spot of Hg is produced.

Presence of Hg(I) is confirmed.

Centrifugate: May contain $[Ag(NH_3)_2]^+$ or H_2WO_4. Add dilute HCl in drops with shaking till a faint precipitate forms, which is re-dissolved by adding one drop of dilute NH_3 solution. Add KI solution drop wise with shaking till precipitation, if any, is complete. Centrifuge.

Residue: Pale yellow precipitate of AgI.

1)To a portion of the above precipitate, add excess of sod. thiosulphate solution. The precipitate dissolves. Presence of Ag^+ confirmed.

2) Spot test: Place a drop of the test solution (original) on a watch glass and add a drop of ammonium carbonate solution and mix. Withdraw a drop of clear liquid from the mixture and place it on a drop reaction paper and add a drop of K_2CrO_4 solution. A red ring is obtained due to formation of Ag_2CrO_4.

Presence of Ag(I) is confirmed.

Centrifugate: Tungstic acid (H_2WO_4) solution.

Reduce to half its volume by evaporation, cool and do the following tests:

1) To 0.5 cm^3 of the solution, add ferrous sulphate solution. A brown precipitate of ferrous tungstate is formed. Add 1 $cm^3$of dilute HCl and boil. The precipitate turns white and then yellow due to formation of tungstic acid.

2) Spot test: Place a drop of the test solution (original) on a drop reaction paper and add a drop of conc. HCl. A drop of saturated $SnCl_2$ solution is placed at the centre of the spot. A blue colour is produced due to formation of tungsten blue, W_2O_5.

Presence of W(VI) is confirmed.

Residue: White – $PbSO_4$.
Dissolve in ammonium acetate solution (or a mixture of NH_3 solution and acetic acid) and the following tests are done:

1) To 1 cm^3 of the solution, add acetic acid and K_2CrO_4 solution. A yellow precipitate of $PbCrO_4$ is formed.

2) To 1 cm^3 of the solution, add KI solution. Boil and cool. A yellow precipitate of PbI_2 is formed, which dissolves on heating and re-precipitates as golden spangles on cooling.

3) Spot test: Place a drop of the solution on a drop reaction paper and add a drop of ammonium sulphide solution. A black spot of PbS is formed.

Presence of Pb (II) is confirmed.

Centrifugate: May contain Tl^+. Add dilute NH_3 solution and boil off excess NH_3. Cool and do the following tests:

1) To 1 cm^3 of the solution, add acetic acid and K_2CrO_4 solution. A yellow precipitate of Tl_2CrO_4 is formed.
2) Flame test: Evaporate 2 $cm^3$of the solution to dryness in a china dish, cool and mix residue with a drop of conc.HCl using a glass rod. A speck of the mixture is taken at the tip of a nickel spatula and introduced into a Bunsen flame. An intense green colour appears
3) **Spot test:** Place a drop of the solution on a drop reaction paper and add a drop sodium thiosulphate solution. Add a drop of KI solution over it. A yellow spot of Tl (I) is produced.

Presence of Tl (I) is confirmed.

Group Classification-2

<table>
<tr><td colspan="2">Wash the Group II residue with 2 cm^3 of a solution of ammonium chloride saturated with H_2S and centrifuge. Discard centrifugate. Transfer residue into a small beaker and add 5 cm^3 of yellow ammonium sulphide (amm. polysulphide) solution. Heat to about 50 to 60^0C and maintain at this temperature for 5 minutes with stirring. If there is a precipitate, cool and centrifuge.</td></tr>
<tr><td rowspan="2">Residue: Black – HgS, PbS, Bi_2S_3 or CuS. Yellow – CdS.

Analyse as given in Table 2A.</td><td>Centrifugate: Add conc. HCl dropwise till just acidic (do not add excess!) and warm while stirring. A fine white or pale yellow precipitate is only sulfur. If a flocculant precipitate is formed, centrifuge. If not, discard the solution.</td></tr>
<tr><td>Residue: Yellow – SnS_2, Se or As_2S_3. Orange red – Sb_2S_3.
Brown -Te, SnS or MoS_3.

Analyse as given in Table 2B.</td></tr>
</table>

Group Classification-2(A)

<table>
<tr><td colspan="5">The Group IIA (Copper Group) residue is washed two times using 2 cm^3 of distilled water and centrifuged. Discard washings. Transfer residue to a small beaker, add 10 cm^3 of dilute nitric acid and boil for 5 minutes. If some solid material remains, cool and centrifuge.</td></tr>
<tr><td>

Residue: Black – HgS.

Dissolve by boiling with 2 cm^3 of aqua regia. Do the following tests with this solution:

1) To 0.5 cm^3 of the solution, add NaOH solution dropwise with shaking till excess. A brownish red precipitate changing to yellow HgO.

2) To 0.5 cm^3 of the solution, add Na_2CO_3 solution dropwise and shake till effervescence just stops. Then add KI solution dropwise with shaking till excess. A red precipitate of HgI_2 is formed, which dissolves in excess reagent.

3) Spot test: Place a drop of the test solution on a spot plate. Add a drop of amm.thiocyanate solution and a drop of cobalt acetate solution. A blue colour is produced.

Presence of Hg(II) is confirmed.

</td><td colspan="4">

Centrifugate: May contain nitrate of Pb, Bi, Cu or Cd. Add dilute H_2SO_4 till precipitation (if any) is complete. Centrifuge.

</td></tr>
<tr><td></td><td>

Residue: White – $PbSO_4$.
Dissolve in ammonium acetate solution (or a mixture of NH_3 solution and acetic acid) and the following tests are done:

1) To 1 cm^3 of the solution, add acetic acid and K_2CrO_4 solution. A yellow precipitate of $PbCrO_4$ is formed.

2) To 1 cm^3 of the solution, add KI solution. Boil and cool. A yellow precipitate of PbI_2 is formed, which dissolves on heating and re-precipitates as golden spangles on cooling.

3) **Spot test:** Place a drop of the solution on a drop reaction paper and add a drop of amm. Sulphide solution. A black spot of PbS is formed.

Presence of Pb(II) is confirmed.

</td><td colspan="3">

Centrifugate: May contain nitrate or sulphate of Bi, Cu or Cd. Add concentrated NH_3 solution dropwise with shaking till smell of ammonia persists. If a residue remains, centrifuge.

</td></tr>
<tr><td colspan="2"></td><td>

Residue: White – $Bi(OH)_2$.
The residue is divided into two parts.

1) To one part of the residue, add a few drops of conc. H_2O_2 solution. A yellowish brown precipitate of bismuthate ions (BiO_3^-) is produced.

2) Dissolve the second part of the residue in 1 cm^3 of dilute HNO_3 and divide into two parts. To one part, add KI solution dropwise with shaking to excess. A black precipitate of BiI_3 is first formed, which dissolves in excess KI to give an orange solution of $[BiI_4^-]$.

3) Spot test: Place a drop of the second part on a spot plate and add a drop of thiourea solution. An intense yellow colour is produced.

Presence of Bi(III) is confirmed

</td><td colspan="2">

Centrifugate: May contain $[Cu(NH_3)_4]^{3+}$ or $[Cd(NH_3)_4]^{3+}$. If deep blue in colour, Cu is present. Add dilute acetic acid with shaking till a clear solution is obtained. Divide into two parts.

</td></tr>
<tr><td colspan="3"></td><td>

Divide the first part into three equal portions and do the following tests:

1) To one part, add pot. Ferrocyanide solution. A reddish brown precipitate of copper ferrocyanide is formed.

2) To the second portion, add pot.thiocyanate solution. A black precipitate turning slowly white is formed.

$$2\ Cu(SCN)_2 \rightarrow 2\ CuSCN + (SCN)_2$$

3) **Spot test:** Place a drop of the third part on a spot plate and add a drop of tartaric acid solution, followed by a drop of NaOH solution. An intense blue colour is produced.

Presence of Cu(II) is confirmed

</td><td>

Divide the second part into three equal portions and do the following tests:

1) To one part, add NaOH solution. A white precipitate of $Cd(OH)_2$ is formed.

2)Through the second portion, pass H_2S. A yellow precipitate of CdS is obtained.

3) Spot test: Place a drop Cadion - 2 B reagent on a drop reaction paper. Place a drop from the third part over it, followed by a drop of KOH solution. A bright pink spot surrounded by a blue circle is produced.

Presence of Cd(II) is confirmed.

</td></tr>
</table>

Group Classification-2(B)

<table>
<tr><td colspan="5">Transfer the Group IIB (Tin Group) residue into a small conical flask and place a funnel in its mouth. Add 5 $cm^3$of conc. HCl and boil gently for 5 minutes. Dilute with 3 $cm^3$of distilled water, cool and centrifuge.</td></tr>
<tr><td colspan="4">Residue: Yellow - Se or As_2S_3. Brown –Te or MoS_3. Dissolve in 5 $cm^3$of conc. HCl containing a pinch of solid potassium chlorate ($KClO_3$). Transfer solution to a small beaker and concentrate by evaporating on a water bath. Cool and add NH_3 solution with stirring till smell of ammonia persists. Add 2 $cm^3$of $Mg(NO_3)_2$ solution and stir for 5 minutes. When precipitation is complete, centrifuge.</td><td>Centrifugate: May contain Sb or Sn as chloride. Boil to expel H_2S. Cool and carry out the following tests using small portions of the solution.</td></tr>
<tr><td>Residue: White crystalline $Mg(NH_4)AsO_4.6H_2O$ Shake the residue well with 3$cm^3$of water and divide into three portions.

1) To one portion, add AgNO3 solution containing a few drops of acetic acid. A red precipitate of silver arsenate, Ag_3AsO_4, is formed.

2) To the second portion, add 0.5 $cm^3$of conc. HNO_3 and excess of amm. molybdate solution. A yellow precipitate of amm. arsenomolybdate is formed.

3) <u>Spot test:</u> To the third portion, add two drops of conc. H_2O_2 solution and warm. Acidify with a few drops of acetic acid. Place a drop of this mixture on a drop reaction paper followed by a drop of $AgNO_3$ solution. A red spot is obtained.

Presence of As
is confirmed.</td><td colspan="2">Centrifugate: May contain Se, Te or Mo as chlorides. Transfer to a small beaker and boil off NH_3. Add 2 $cm^3$of conc. HCl and evaporate to half volume on a water bath. Add 2 $cm^3$of a saturated solution of sodium sulphite (Na_2SO_3) solution. If a precipitate is formed, centrifuge.

Residue: Red – Se.
Dissolve the residue by heating with 1 cm^3 of conc. HNO_3. Neutralise by adding amm. carbonate solution dropwise till effervescence stops.
Divide the solution into three parts.

1) To one part, add $BaCl_2$ solution. A white precipitate of $BaSeO_3$ is formed.

2) To the second part, add $CuSO_4$ solution. A bluish green precipitate of $CuSeO_3$ is formed.

3) <u>Spot test:</u> Place a drop of the third portion on a spot plate and add a drop of thiourea solution. A red precipitate of Se is formed.

Presence of Se (IV)
is confirmed.</td><td>Centrifugate: Dilute with equal volume of water. Add 1 $cm^3$of KI solution and a drop of sodium sulphite (Na_2SO_3) solution. If a precipitate is formed, centrifuge

Residue: Black – Te
Dissolve in 2 $cm^3$of cold dilute HCl. Divide the solution into three parts.

1) Neutralise one portion by adding amm. carbonate solution dropwise till effervescence stops. Add $BaCl_2$ solution. A white precipitate of $BaTeO_3$ is formed.

2) To the second part, add excess of KI solution. A red colour is produced due to formation of $[TeI_6]^{2-}$.

3) <u>Spot test</u>: Place a drop of the third portion on a spot plate and add a drop of 50% hypophosphorus acid. Evaporate. A black stain due to Te is seen.

Presence of Te (IV)
is confirmed.</td><td>Centrifugate: Add 1 cm^3 of conc. HCl and boil to remove dissolved SO_2.Divide the solution into three parts.

1) To one part, add pot.ferrocyanide solution. A reddish brown precipitate of Mo ferrocyanide is formed.

2) To the second part, add two drops of ferroussulphate solution. A blue colour is produced.

3) <u>Spot test</u>: Place a drop of the third portion on a drop reaction paper and add a drop of pot. Thiocyanate solution. Then add a drop of $SnCl_2$ solution. A red spot of $[Mo(SCN)_6]^{3-}$ is seen.

Presence of Mo (VI)
is confirmed.</td><td>To 2 $cm^3$of the solution in a test tube, add a pinch of iron filings and boil to reduce Sn(IV) to Sn(II). Cool and centrifuge. With draw the clear supernatant carry out the following tests.

1) to 1 cm^3 of the solution in a test tube, add two drops of mercuric chloride ($HgCl_2$) solution. A silky white or grey precipitate of Hg_2Cl_2 is obtained.

2) To 0.5 $cm^3$of the solution in a test tube, add NaOH solution dropwise with shaking. A white precipitate of $Sn(OH)_2$ soluble in excess NaOH is obtained.

3) <u>Spot test</u>: Place a drop of the solution on a drop reaction paper and add a drop of bismuth nitrate and a drop of NaOH solution. A black spot due to Bi metal.

Presence of Sn
is confirmed.</td><td>To 1 $cm^3$of the solution in a test tube, add just enough NH_3 solution to neutralize. (A slight precipitation may occur). Add a pinch of solid oxalic acid and boil. Pass H_2S through the solution. An orange precipitate of Sb_2S_3 is obtained.

<u>Spot test</u>: Place a drop of the solution on a spot plate and add a minute crystal of sodium nitrite ($NaNO_2$) . Then add a drop of rhodamine- B reagent. A blue colour is obtained.

Presence of Sb
is confirmed.</td></tr>
</table>

Group Classification-5(B)

The Cations of this group are generally water soluble, hence they are detected from the water extract. Water is prepared by boiling 0.2g of the mixture with 1 cm^3 of water. It is centrifuge after cooling and the centrifugate is used as follows.

For lithium

1) **Flame test**: To two drops of the test solution in a china dish, add a drop of conc. HCl and evaporate to dryness. Take a speck of the dry residue at the tip of a charred match stick and introduce into a colourless Bunsen flame near the base. The flame is coloured carmine red, indicating Li.
2) **Spot test**: Place a drop of the test solution on a spot plate. Add a drop of NaCl solution and a drop of ferric periodate reagent. A white precipitate of $KLiFe[IO_6]$ is formed.

Presence of Li(I) is confirmed.

For Potassium

1. Take 5-6 drops of water extract and add 0.5 cm^3 of 4N NaOH solution to it .Boil strongly to remove NH_4^+ as NH_3 gas, cool the solution and used as follows

   Acidify 2-3 drops of solution with 4N CH_3COOH and add 3-4 drops of 5% $Na_2Co(NO_2)_6$ solution to it .shake well and allow it to stand for about 10-15 sec – A yellow Crystalline Ppt

   , K^+ Present

   C.T.

   a) 3 drops of the solution (free from NH_3) are treated with 4-5 drops of saturated picric acid solution .On shaking Well a - A yellow Crystalline Ppt

   b) 2 drops of the solution (free from NH_4^+) + 3-4 drops of 50% EtOH + 4-5 drops of saturated tartaric acid solution – White Ppt

Spot Test : A drop of solution on a paper containing 1% Dipicryl amine reagent – orange red spot developed

For Sodium

Flame Test : Perform flame test with the mixture- Golden Yellow Flame

Na^+ Confirm

SPECIAL TEST FOR SOME POSITIVE IONS

Rare Cation	Reagent / Spot Test	Observation	Inference
NH_4^+ (Ammonium)	NaOH solution, warm	Pungent smell of NH_3; moist red litmus turns blue	NH_4^+ present
Pb^{2+} (Lead)	Potassium chromate (K_2CrO_4)	Yellow precipitate	Pb^{2+} present
Cu^{2+} (Copper)	NH_4OH (excess)	Deep blue solution	Cu^{2+} present
Bi^{3+} (Bismuth)	Thiourea in acidic medium	Yellow to orange colour	Bi^{3+} present
Cd^{2+} (Cadmium)	H_2S in acidic medium	Bright yellow precipitate	Cd^{2+} present
Hg^{2+} (Mercuric)	KI solution	Scarlet-red precipitate of HgI_2 (soluble in excess KI)	Hg^{2+} present
As^{3+} / As^{5+} (Arsenic)	H_2S in acidic medium	Yellow precipitate	Arsenic present
Sb^{3+} (Antimony)	H_2S in acidic medium	Orange precipitate	Antimony present
Sn^{2+} / Sn^{4+} (Tin)	$HgCl_2$ solution	White precipitate turning grey/black	Tin present

SPECIAL TEST FOR SOME RARE POSITIVE IONS

Ion	Procedure (How to Perform the Test)	Observation	Inference
Tl^{+} (Thallium)	Take **2 mL original solution (O.S.)** in a test tube. Add **2–3 drops of KI solution** and shake.	**Bright yellow precipitate** of TlI forms, insoluble in excess KI.	Tl^{+} present.
W (Tungsten, WO_4^{2-})	Take **2 mL O.S.** Acidify with **dilute HCl**. Add **2–3 drops of freshly prepared $SnCl_2$ solution** (or a small piece of zinc). Shake gently.	**Deep blue colour** (Tungsten Blue) appears.	Tungsten present.
Se (Selenium, SeO_3^{2-}/SeO_4^{2-})	Take **2 mL O.S.** Acidify with **dilute HCl** add **fresh $SnCl_2$ solution** and warm gently.	**Brick-red precipitate** of elemental selenium appears.	Selenium present.
Te (Tellurium, TeO_3^{2-}/TeO_4^{2-})	Take **2 mL O.S.** Acidify with **dilute HCl** and add **fresh $SnCl_2$ solution**. Warm gently if required.	**Black precipitate** of elemental tellurium appears.	Tellurium present.
Mo (Molybdenum, MoO_4^{2-})	Take **2 mL O.S.** Add **1 mL dilute HCl**, then **2–3 drops of NH_4SCN solution**, followed by **2–3 drops of freshly prepared $SnCl_2$ solution**. Mix well.	**Deep blood-red colour** develops due to thiocyanato-molybdenum complex.	Molybdenum present.
Li^{+} (Lithium)	Clean a **platinum/nichrome wire** by dipping it in concentrated HCl and heating until no colour is seen. Dip the wire into the sample and place it in the **non-luminous Bunsen flame**. Observe the flame colour.	**Crimson (carmine) red flame**.	Li^{+} present.