EXPERIMENTAL INORGANIC CHEMISTRY

For B.Sc. and M.Sc. Students
As per new Syllabus

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Dedicated to all
our beloved
graduates & post graduate
students

INORGANIC PREPARATION

1. TETRAMINE CUPRIC SULPHATE, $[Cu(NH_3)_4]SO_4 \cdot H_2O$

(A) REAGENTS

Cupric sulphate, Ammonia, Ethyl alcohol, Nitric acid, Distilled water, Sulphuric acid.

(B) REACTION

$$CuSO_4 \cdot 5H_2O_{(aq)} + 4NH_{3(aq)} \longrightarrow [Cu(NH_3)_4]SO_4 \cdot H_2O + 4H_2O$$

(C) PROCEDURE

Take 5 gm crystalline cupric sulphate in a 250 ml beaker. Dissolve it in minimum quantity of water and then add few drops of diluted sulphuric acid. Add concentrated ammonia solution to the beaker with constant stirring, until the blue precipitate of cupric hydroxide, first formed completely dissolve to yield a clear, deep blue solution and there should be smell of ammonia in the beaker. Now add 20 ml alcohol dropwise from the dropping funnel to the beaker with constant stirring until the blue precipitates settled and clear solution is obtained. Heat it to 60o 70oC in the water bath for about 10-15 minutes. Then stop heating and remove the beaker from the water bath and allow it to stand. Long needle shaped blue crystals of tetramine cupric sulphate separates out. Filter and wash the crystals with a few drops of alcohol. Dry the crystals on a porous plate or in a desiccator. Weigh the dry crystal and find out the percentage yield followed by percentage purity by usual methods.

2. TRI (THIOUREA)-CUPROUS SULPHATE, $[Cu(NH_2CSNH_2)_3]_2SO_4 \cdot 2H_2O]$

(A) REAGENTS

Cupric sulphate, Ethyl alcohol, Nitric acid, Thiourea, Distilled water, Ammonia.

(B) REACTION

$$2CuSO_4 \cdot 5H_2O_{(aq)} + 6NH_2CSNH_{2(aq)} + H_2O \longrightarrow [Cu(NH_2CSNH_2)_3]_2SO_4 \cdot 2H_2O_{(aq)} + 4H_2O + SO_2 + O_2$$

(C) PROCEDURE

Dissolve 8 gm of crystalline cupric sulphate in 40 ml of water. And dissolve 8 gm of thiourea in 20 ml of warm water in another beaker and cool it to room temperature. To the solution of copper sulphate add thiourea solution with constant stirring and cool this mixture to the running water until the separated yellowish oil sticks to the wall of the containing beaker keep the beaker for sometimes in running water and separate the oil from the mother liquid by decantation. Take 4 gm of thiourea in another beaker and dissolve in 40 ml of hot water and cool it to room temp. Shake the oil with this solution of thiourea until the crystallization is complete. Separate the crystals from the mother liquor by filtration and wash them with small volume of water. The crystals are recrystallized from 5% aqueous thiourea solution containing 2 ml of normal sulphuric acid per 100ml of solution. During recrystalisation temperature must be kept below 80_oC. Dry the crystals on a porous plate or in a desiccators. Weigh the dry crystal and find out the percentage yield followed by percentage purity by usual methods.

3. TRI (THIOUREA) CUPROUS CHLORIDE, $[Cu(NH_2CSNH_2)_3]Cl$

(A)REAGENTS

Copper sulphate, Ethyl alcohol, Distilled water, Thiourea, Sulphuric acid, Ammonia.

(B)REACTION

$$2\,Cu\text{–}Turning_{(s)} + 3NH_2CSNH_{2(aq)} + HCl \longrightarrow [Cu(NH_2CSNH_2)]_3Cl + \tfrac{1}{2}\,H_{2(g)}\uparrow$$

(C)PROCEDURE

Dissolve 5 gm of Thiourea in 25 ml hot water. Add 1 gm of copper turning and than 5 ml of concentrated hydrochloric acid in the beaker. Heat on the water bath, copper dissolves with the liberation of hydrogen. Filter while hot and then allow it to cool, crystals of the complex will separate out. Filter and wash with acetone. The white elongated crystals are opaque and presented porcelain like appearance. Then consist in fact of oriented aggregates of much smaller transparent true crystals. Recrystallize it from 5 % aqueous thiourea solution and then acidified with a small amount of hydrochloric acid, the complex chloride is seen as well formed square(tetragonal) prisms terminated by a square pyramid.Dry the crystals on a porous plate or in a desiccator. Weigh the dry crystal and find out the percentage yield followed by percentage Purity by usual methods.

4. HEXAMMINE NICKEL(II) CHLORIDE, $[Ni(NH_3)_6]Cl_2$

(A) REAGENTS

Nickel Chloride, Ammonia , 10 pH buffer solution, Distilled water.

(B) REACTION

$$NiCl_2{\cdot}6H_2O_{(aq)} + 6NH_{3(aq)} \longrightarrow [Ni(NH_3)_6]Cl_{2(s)} + 6H_2O$$

(C) PROCEDURE

Dissolve 12 gm of nickel chloride in 20 ml of warm water. Filter the solution to remove any insoluble impurities. Add about 40 ml of aqueous ammonia slowly to the solution (stirred rapidly) until the green precipitate of nickel hydroxide dissolved. Allow the mixture to stand at room temperature for 30 min. and then remove the crystals of hexa ammine nickel chloride by filtration. Wash the precipitate with ammonia then wash it with acetone and allow the product to dry at room temperature. Dry the crystals on a porous plate or in a desiccator. Weigh the dry crystal and find out the percentage yield followed by percentage Purity by usual methods.

5. HEXA (THIOUREA) – PLUMBUS NITRATE, $[Pb(NH_2CSNH_2)_6](NO_3)_2$

(A) REAGENTS

Lead nitrate, Thiourea, Nitric acid, Hydrochloric Acid, Distilled water

(B) REACTION

$$Pb(NO_3)_{2(aq)} + 6NH_2CSNH_{2(aq)} \rightarrow [Pb(NH_2CSNH_2)_6](NO_3)_{2(s)}$$

(C) PROCEDURE

Prepare the solution of 3 gm lead nitrate in 10 ml of hot water and 4.5 gm of Thiourea in 15 ml of hot water. Now mix both the two solutions. Boil the resultant solution for 1 - 2 minute and then allow it to cool. When colorless, needle shaped crystals separates, filter and collect it. Recrystallize the crystals from 25 ml water containing 5 ml of 1 N Nitric acid when colorless small orthorhombic prisms of Hexa Thiourea Plumbus Nitrate separates out. Dry the crystals on a porous plate or in a desiccator. Weigh the dry crystal and find out the percentage yield followed by percentage Purity by usual methods.

6. POTASSIUM TRIOXALATO CHROMATE(III), $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$

(A) REAGENTS

Potassium oxalate, Oxalic acid, Potassium dichromate, Ethyl alcohol(Ethanol).

(B) REACTION

$$2K_2C_2O_{4(aq)} + 4H_2C_2O_{4(aq)} + K_2Cr_2O_{7\,(aq)} \rightarrow 2K_3[Cr(C_2O_4)_3]_{(s)} + 7H_2O$$

(C) PROCEDURE

Prepare a solution of 9 gm of oxalic acid in 20 ml of warm water and then add 3 gm of potassium dichromate when the vigorous action has subsided. Heat the resulting solution to boiling, dissolve 3.5 gm of potassium oxalate in it. Cool the whole solution below 10^0C temperature. Add 3 to 4 ml of Ethanol to the cool solution, blue green crystal will soon separate out from an almost black solution. Filter the product and collected product is then washed first with an equal volume of ethanol and water, followed by Ethanol. Long blue prisms like crystals are obtained. Dry the crystals on a porous plate or in a desiccator. Weigh the dry crystals and submit to your teacher and find out the percentage yield. Dry the crystals on a porous plate or in a desiccator. Weigh the dry crystal and find out the percentage yield followed by percentage Purity by usual methods.

7. POTASSIUM TRIOXALATO ALUMINATE

$K_3[Al(C_2O_4)_3]$

(A) REAGENTS

Aluminum sulphate, Sodium hydroxide, Oxalic acid, Potassium oxalate, Potassium hydroxide,Sulphuric acid.

(B) REACTION

$$Al_2(SO_4)_3\cdot 16H_2O_{(aq)} + 6NaOH_{(aq)} \rightarrow 2Al(OH)_{3(s)} + 3Na_2SO_{4(aq)} + 16H_2O$$

$$2Al(OH)_{3(s)} + 3H_2C_2O_{4(aq)} + 3K_2C_2O_{4(aq)} \rightarrow 2K_3[Al(C_2O_4)_3] + 6H_2O$$

(C) PROCEDURE

Dissolve 7 gm of aluminum sulphate in 100 ml water. Add 2.5 gm sodium hydroxide in 20 ml of water in another beaker. Now mix both the solution with constant stirring, aluminum hydroxide

will be precipitated. Filter this precipitate and wash with water. Now take 4 gm of oxalic acid and 6 gm of potassium oxalate in 100 ml of water and add aluminum hydroxide precipitate to this solution and then boil it. Filter hot, discard any unreacted aluminum hydroxide precipitates. Evaporate the filtrate to crystallization, orthorhombic crystal of the potassium trioxalato aluminate will be obtained. Dry the crystals on a porous plate or in a desiccator. Weigh the dry crystal and find out the percentage yield followed by percentage Purity by usual methods.

8. SODIUM TRIOXALATO FERRATE(III), $Na_3[Fe(C_2O_4)_3]\cdot 3H_2O$

(A) REAGENTS

Ferric chloride, Sodium hydroxide, Oxalic acid, Potassium hydroxide, Zn-dust, Sulphuric acid

(B) REACTION

$$FeCl_{3(aq)} + 3NaOH_{(aq)} \rightarrow Fe(OH)_{3(s)} + 3NaCl$$

$$Fe(OH)_{3(s)} + 3H_2C_2O_{4(aq)} + NaOH + 3H_2O \rightarrow Na_3[Fe(C_2O_4)_3]\cdot 9H_2O$$

(C) PROCEDURE

Dissolve 10 gm of ferric chloride in 10 ml water and in another beaker dissolve 7.3 gm of sodium hydroxide in 5 ml water. Now to the solution of ferric chloride add sodium hydroxide solution slowly, resulting in the formation of ferric hydroxide. Now filter the precipitate of ferric hydroxide through Buckner funnel and wash with small quantities of hot water. Dissolve 12 gm of oxalic acid in 50 ml of water. To this solution add the pellets of 4 gm sodium hydroxide, resulting in the formation of sodium oxalate. Now add the washed hydrated ferric oxide to the hot sodium oxalate solution with constant stirring. Filter the solution and reject any residue if present on the filter paper. Evaporate the green filtrate on a water bath to get the green crystals of sodium trioxalato ferrate. Wash these crystals first with ice cold water and followed by alcohol. Dry the crystals on a porous plate or in a desiccator. Weigh the dry crystal and find out the percentage yield followed by percentage Purity by usual methods.

9. HEXAMMINO COBALTIC CHLORIDE, $[Co(NH_3)_6]Cl_3$

(A) REAGENTS

Cobalt Chloride, Ammonium Chloride, Charcoal, Hydrogen peroxide, Hydrochloric Acid, Hexamine, Distilled water

(B) REACTION

$$CoCl_2\cdot 6H_2O_{(aq)} + NH_4Cl_{(aq)} + H_2O_{2(aq)} + 5\,NH_{3(aq)} \rightarrow [Co(NH_3)_6]\,Cl_{3(s)} + 8H_2O$$

(C) PROCEDURE

Dissolve 12 gm ammonium chloride and 18 gm cobalt chloride in 25 ml of boiling water. Add 1gm decolorizing charcoal and cool it in ice. Add 40 ml agues ammonia solution and keep the solution at 10^oC or lower. Add slowly in small portions 35 ml 20 volume hydrogen peroxide. Shake the solution during addition. Gradually raise the temperature to 50 to 60^o C and keep the flask at this temperature with frequent shaking until the last trace of pink coloration is removed. Cool and filter. Transfer the crystals to a beaker and dissolve it in 150 ml of boiling water containing 5 ml con.HCl. When the entire solid, except the charcoal dissolves, filter the liquid

while hot. Add 20 ml concentrate HCl to the filter and cool the solution in ice. Collect the golden brown crystals wash with acetone and dry. If necessary the complex may be recrystallised from water contain a trace of hydrochloric acid. Dry the crystals on a porous plate or in a desiccator. Weigh the dry crystal and find out the percentage yield followed by percentage Purity by usual methods.

10. PENTA THIOUREA DICUPROUS NITRATE

$[Cu\ (NH_2CSNH_2)_5]\ (NO_3)_2$

(A) REAGENTS

Cupric carbonate, Thiourea, Ammonia, Sulphuric acid, Nitric acid, Distilled water.

(B) REACTION

$$CuCO_3\,Cu(OH)_2{\cdot}H_2O_{(s)} + 6NH_2CSNH_{2(aq)} + 2HNO_3 + H_2O \rightarrow [Cu_2(NH_2CSNH_2)_5]\ (NO_3)_{2(s)} + 3H_2O + 2CO_2 + 2NH_3 + S$$

(C) PROCEDURE

Mix 4gm of cuprous carbonate in 20ml distilled water in a beaker. To this add concentrated nitric acid with constant stirring till all copper carbonate just dissolves and a green colored solution is obtained. Dissolve 10 gm of Thiourea in 100 ml of hot distilled water in another beaker. To this add copper solution with stirring. The resulting mixture is at first clear and yellowish in color, but on heating for about 90 minutes on a water bath sulphur separates out. (It reduces Cu^{+2} To Cu^{+}). Filter quickly, while the solution is hot. (Reject the residue of free sulphur). When the filtrate is cooled needle shaped crystals of cuprous nitrate complex separates out which are filtered washed with a little volume of water and dried. Weight the dried sample as penta thiourea dicuprous nitrate. Dry the crystals on a porous plate or in a desiccator. Weigh the dry crystal and find out the percentage yield followed by percentage Purity by usual methods.

11. IRON(III) ACETYLACETONATE

$Fe(acac)_3$ / $Fe(C_5H_7O_2)_3$

(A) REAGENTS

Iron(III) chloride, Zn-dust, Potassium Hydroxide, Acetylacetone, Nitric Acid.

(B) REACTION

$$FeCl_{3(aq)} + 3KOH_{(aq)} \rightarrow Fe\ (OH)_{3(s)} + 3KCl_{(aq)}$$

$$Fe\ (OH)_{3(s)} + 3C_5H_7O_2 \rightarrow Fe\ (acac)_3 + 3H_2O$$

Green Principles: The preparation is an example of atom economy, Produces no waste and Requires no organic solvents

(C) PROCEDURE

Iron(III) chloride (15g, 92.48mmol) was dissolved in 200 ml of water in a 500 ml beaker followed by addition of 20% aqueous solution of KOH (83.13 ml, 296.31 mmol) in parts with constant stirring to precipitate the metal as its hydroxide. The suspended precipitate was allowed to settle with the supernatant liquid becoming colorless. The flocculent was washed several times with

water by decantation, finally by filtration through Whatman No. 42 filter paper and again washing twice with cold water. Then the precipitate was quantitatively transferred into a 250 ml beaker and the whole was kept on ice water bath for 15min. distilled acetylacetone (30.55ml, 295.91mmol) was added
to the slurry and mixed thoroughly with a glass rod. The whole mixture was continued to stand on ice water bath for 30 min with occasional stirring. An exothermic reaction sets in leading to the formation of deep red shiny crystals of Iron(III) acetylacetonate, $Fe(acac)_3$. the reaction container was then placed in an ice water bath for 15 min. the compound was filtered through Whatman No.42 filter paper and dried *in vacuo* over fused $Cacl_2$. yield: 28.6g, 80.97mmol (87.56%) Mp 180-181^{0}C.Dry the crystals on a porous plate or in a desiccator. Weigh the dry crystal and find out the percentage yield followed by percentage Purity by usual methods.

12. PRUSSIAN BLUE

$Fe_4[Fe(CN)_6]_3$

(A) REAGENTS

Iron fillings 0.5 gm, Ethyl alcohol 15ml, Potassium Ferrocyanide 4.5 gm, Sulphuric acid 50 ml.

(B) REACTION

$$4FeCl_{3(aq)} + 3K_4[Fe(CN)_6] \rightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$$

(C) PROCEDURE

Take 0.5 gm of Iron filling in one becker, add 10ml of dil. H_2SO_4 in it. Heat it and as soon as reaction becomes vigrous, remove the burner and cool the solution, Filter it. Again add 10 ml.dil. H_2SO_4 in it and repeat the procedure. Collect the filtrates in a 250 ml beaker. To it add a saturated solution of 4.5 gm.of potassium ferrocynide. Heat the solution until it acquires green colour. Keep the green colored product in air for nearly two hours. When it changes to blue. (You can pass the air through the green colloured product .Dry the crystals on a porous plate or in a desiccator. Weigh the dry crystal and find out the percentage yield followed by percentage Purity by usual methods.

ESTIMATIONS

Estimation of some metal ions by EDTA titration

(A) Direct Titration

(1) Copper: Take 1 gm of complex salt exactly in an evaporating dish. Add 5 ml con. nitric acid and evaporate it to nearly dryness, repeat this. Dissolve residue in distilled water, make it 250 ml in measuring flask. Take 25 ml of stock solution in conical flask. Add 10 ml ammonia to make it alkaline and add few drops of Fast Sulphone Black-F indicator. Titrate it against 0.05 M EDTA solution, until the color changes from blue to dark green. Repeat it until constant reading. Tabulate your results.

Observation Table

Burette Reading	Pilot Reading				Average
End point					
Initial					
Difference					B ml

Calculation

(a) Theoretical Purity

M.W. of the Prepareparation = M.W. of the metal ion

Weight taken for the estimation = ?

327 = 63.5 gm Cu
For $[Cu(NH_2CSNH_2)_3]Cl$

1 gm = 19.42 g Cu

(b) Practical Purity

1000 ml 1 M EDTA = 63.5 g Cu
1000 ml 0.05 M EDTA = 3.175 g Cu

B ml 0.05 M EDTA (Burrette Reading) $= \frac{3.175 \times B}{1000}$ **(Cu present in 25ml)**

$= \frac{3.175 \times B \times 10}{1000}$ **(Cu present in 250ml)**

(c) % Purity $= \frac{\text{Practical Purity}}{\text{Theoretical Purity}} \times 100$

= _____ %

(2) Nickel :
Take exactly 1 gm of complex salt in an evaporating dish. Add 5 ml of concentrated nitric acid and evaporate it to nearly dryness. Dissolve residue in a distilled water. Make it 250 ml in measuring flask. Take 25 ml of diluted solution in conical flask. And dilute with 150 ml distilled water, add buffer solution make it alkaline. Add few drops of Bromopyrogallol Red indicator. Titrate it against 0.05 M EDTA solution, until the color changes from blue to claret red. Repeat it until constant reading. Tabulate your results. Find out the yield and percentage purity.
(3) Lead :
Take 1 gm complex salt exactly in an evaporating dish. Add 5 ml of concentrated nitric acid and evaporate it to nearly dryness. Dissolve residue in a distilled water. Make it 250 ml in measuring flask. Take 25 ml diluted solution in a conical flask, add hexamine buffer excess the pH 6.0 Add Xylenol Orange indicator. Titrate it against 0.05 M EDTA solution, until color changes from wine red to yellow. Repeat it until constant reading. Tabulate your results. Find out the yield and percentage purity.
(5) Cobalt :
Take 1 gm complex salt exactly in an evaporating dish. Add 5 ml of concentrated nitric acid and evaporate it to nearly dryness. Dissolve residue in a distilled water. Make it 250 ml in measuring flask. Take 25 ml of diluted solution in conical flask, add 50 ml distilled water. Add 1-2 g of hexamine to maintain pH 6, and add few drops of Xylenol Orange. Titrate against 0.05 M EDTA solution. Color change from red to yellow. Repeat it until constant reading. Tabulate your results. Find out the yield and percentage purity.
(5) Iron(III) : Take 1 gm complex salt exactly in an evaporating dish. Add 5 ml of concentrated nitric acid and evaporate it to nearly dryness. Dissolve residue in a distilled water. Make it 250 ml in measuring flask. Take 25 ml of diluted solution in conical flask, add 50 ml distilled water. Addjust the pH to 2-3, and add few drops of Varamine blue (1 gm VB in 100ml DM water), warm the conent to 40°C. Titrate against 0.05 M EDTA solution. Color change from blue to gray just before end point and with final drop of reagent changes to yellow. Repeat it until constant reading. Tabulate your results. Find out the yield and percentage purity

(B) Back Titraion

(1) Chromium:
Take 1 gm complex salt exactly in an evaporating dish. Add 5 ml of concentrated nitric acid and evaporate it to nearly dryness. Dissolve residue in a distilled water. Make it 250 ml in measuring flask. Take 25 ml diluted solution in a conical flask add 25 ml 0.01 M EDTA solution, then add Hexamine buffer to adjust the pH 5 to 6. Add Xylenol Orange indicator, excess of EDTA is titrate against 0.1 M Pb $(NO_3)_2$ solutions. Color change brownish orange to red. Repeat it until constant reading. Tabulate your results. Find out the yield and percentage purity. Find out the yield and percentage purity. (Here 25 ml - Burrett reading = Bml)
(2) Aluminium:
Take 1 gm complex salt exactly in an evaporating dish. Add 5 ml of concentrated nitric acid and evaporate it to nearly dryness. Dissolve residue in a distilled water. Make it 250 ml in measuring flask. Take 25 ml of diluted solution in a conical flask and add 0.01 M 25 EDTA solution, boil the sol`n for few min. to ensure the complete complexation of the Al; cool to room temperature, and add ammonia solution to adjust the pH 7-8. Add Eriochrome Black T indicator and titrate rapidly against 0.01 M $ZnSO_4$, color change blue to wine red. After standing for a few min. the fully titrated solution acquires a reddish violet color due to the transformation of the zinl dye complex into the aluminium – Eriochrome Black T complex; this change is irreversible , so that over titrataed solution are lost. Repeat it until constant reading. Tabulate your results. Find out the yield and percentage purity. (Here 25 ml -Burrett reading = B ml)

Estimation of Fe(II) volumetrically:

Take 1 gm complex salt exactly in an evaporating dish. Add 5 ml of concentrated nitric acid and evaporate it to nearly dryness. Dissolve residue in a distilled water. Make it 250 ml in measuring flask. Take 25 ml of this diluted solution in a conical flask, add Zn dust and 20 ml diluted H_2SO_4 – heat it to Covert Fe^{+3} into Fe^{+2} (test with KCNS, gives red color) cool and filter wash with H_2O, discard the residue and then titrate it against 0.05 N $KMnO_4$ solution. End point gives light pink color. Repeat it until constant reading. Tabulate your results. Find out the yield and percentage purity.