

# **EXPERIMENTAL INORGANIC CHEMISTRY**

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

*Dr. M.K.Shah*

Dedicated to all  
our beloved  
graduates & post graduate  
students

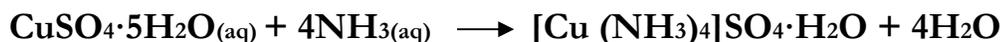
***INORGANIC  
PREPARATION***

## 1. TETRAMINE CUPRIC SULPHATE, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$

### (A) REAGENTS

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

### (B) REACTION



### (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, $[\text{Cu}(\text{NH}_2\text{CSNH}_2)_3]_2 \text{SO}_4 \cdot 2\text{H}_2\text{O}$

### (A) REAGENTS

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

### (B) REACTION



### (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 recrystallisation temperature must be kept below 80oC. 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, $[\text{Cu} (\text{NH}_2\text{CSNH}_2)_3] \text{Cl}$

#### (A) REAGENTS

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

#### (B) REACTION



#### (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, $[\text{Ni} (\text{NH}_3)_6] \text{Cl}_2$

#### (A) REAGENTS

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

#### (B) REACTION



#### (C) PROCEDURE

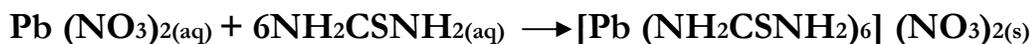
Dissolve 12 gm of nickel chloride in 20 ml of warm water. Filter the solution to remove any insoluble impurities. Add about 40 ml of aqueous ammonia slowly to the solution (stirred rapidly) until the green precipitate of nickel hydroxide dissolved. Allow the mixture to stand at room temperature for 30 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, $[\text{Pb}(\text{NH}_2\text{CSNH}_2)_6] (\text{NO}_3)_2$

#### (A) REAGENTS

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

#### (B) REACTION

**(C) PROCEDURE**

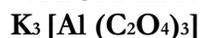
Prepare the solution of 3 gm lead nitrate in 10 ml of hot water and 4.5 gm of Thiourea in 15 ml of hot water. Now mix both the two solutions. Boil the resultant solution for 1 - 2 minute and then allow it to cool. When colorless, needle shaped crystals separates, filter and collect it. Recrystallize 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),  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$** **(A) REAGENTS**

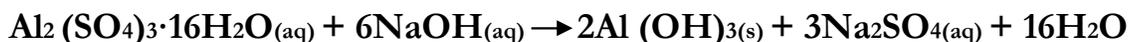
Potassium oxalate, Oxalic acid, Potassium dichromate, Ethyl alcohol(Ethanol).

**(B) REACTION****(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°C 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****(A) REAGENTS**

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

**(B) REACTION****(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

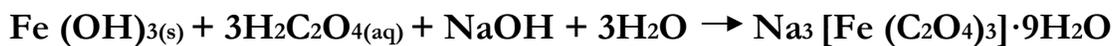
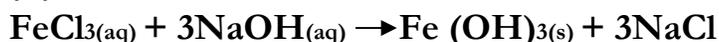
will be precipitated. Filter this precipitate and wash with water. Now take 4 gm of oxalic acid and 6 gm of potassium oxalate in 100 ml of water and add aluminum hydroxide precipitate to this solution and then boil it. Filter hot, discard any unreacted aluminum hydroxide precipitates. Evaporate the filtrate 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), $\text{Na}_3 [\text{Fe} (\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$

### (A) REAGENTS

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

### (B) REACTION



### (C) PROCEDURE

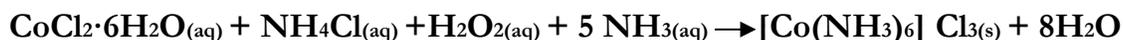
Dissolve 10 gm of ferric chloride in 10 ml water and in another beaker dissolve 7.3 gm of sodium hydroxide in 5 ml water. Now to the solution of ferric chloride add sodium hydroxide solution slowly, resulting in the formation of ferric hydroxide. Now filter the precipitate of ferric hydroxide through 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, $[\text{Co} (\text{NH}_3)_6]\text{Cl}_3$

### (A) REAGENTS

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

### (B) REACTION



### (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 aqueous ammonia solution and keep the solution at 10°C 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°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.

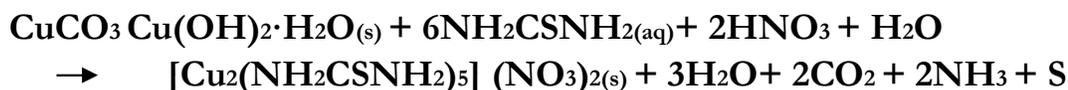
## 10. PENTA THIOUREA DICUPROUS NITRATE



### (A) REAGENTS

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

### (B) REACTION



### (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  $\text{Cu}^{+2}$  To  $\text{Cu}^+$ ). 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.

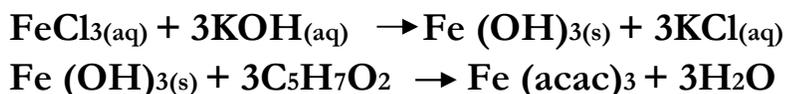
## 11. IRON(III) ACETYLACETONATE



### (A) REAGENTS

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

### (B) REACTION



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

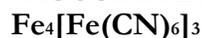
### (C) PROCEDURE

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,  $\text{Fe}(\text{acac})_3$ . 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  $\text{CaCl}_2$ . yield: 28.6g, 80.97mmol (87.56%) Mp 180-181°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.

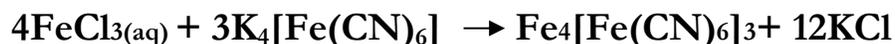
## 12. PRUSSIAN BLUE



### (A) REAGENTS

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

### (B) REACTION



### (C) PROCEDURE

Take 0.5 gm of Iron filling in one becker, add 10ml of dil.  $\text{H}_2\text{SO}_4$  in it. Heat it and as soon as reaction becomes vigorous, remove the burner and cool the solution, Filter it. Again add 10 ml.dil.  $\text{H}_2\text{SO}_4$  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

$$\text{M.W. of the Preparation} = \text{M.W. of the metal ion}$$

$$\text{Weight taken for the estimation} = ?$$

$$\frac{327}{\text{For } [\text{Cu} (\text{NH}_2\text{CSNH}_2)_3] \text{Cl}} = 63.5 \text{ gm Cu}$$

$$1 \text{ gm} = 19.42 \text{ g Cu}$$

#### (b) Practical Purity

$$1000 \text{ ml } 1 \text{ M EDTA} = 63.5 \text{ g Cu}$$

$$1000 \text{ ml } 0.05 \text{ M EDTA} = 3.175 \text{ g Cu}$$

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

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

#### (c) % Purity

$$= \frac{\text{Practical Purity}}{\text{Theoretical Purity}} \times 100$$

$$= \underline{\hspace{2cm}} \%$$

**(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. Adjust the pH to 2-3, and add few drops of Varamine blue (1 gm VB in 100ml DM water), warm the content 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  $\text{Pb}(\text{NO}_3)_2$  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  $\text{ZnSO}_4$ , 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 titrated 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  $\text{H}_2\text{SO}_4$  – heat it to Covert  $\text{Fe}^{+3}$  into  $\text{Fe}^{+2}$  (test with KCNS, gives red color) cool and filter wash with  $\text{H}_2\text{O}$ , discard the residue and then titrate it against 0.05 N  $\text{KMnO}_4$  solution. End point gives light pink color. Repeat it until constant reading. Tabulate your results. Find out the yield and percentage purity.

INORGANIC  
QUALITATIVE  
ANALYSIS

## INTRODUCTION

Discussion of cations and anions in presence of some less common ions (so-called 'rarer' elements) which have greater importance in industrial and analytical use. The elements have been classified, into so far as is possible, in the simple groups with which the reader is familiar, and methods of separation have been indicated.

**Following are the notes to help the student to do his work well, and to obtain his/her results in such a way as to give satisfaction to himself/herself and the instructor.**

- |  |                       |
|--|-----------------------|
| 01. Cleanliness and Tidiness                   | 08. Disposal of waste |
| 02. Risk of fire                               | 09. Accidents         |
| 03. Waste of Gas and chemicals                 | 10. Excess of reagent |
| 04. Removal of the precipitate from the filter | 11. Ignition tubes    |
| 05. Mounting and use of platinum wire          | 12. The wash-bottle   |
| 06. Entering Results in Note book              | 13. The blowpipe      |
| 07. Filtering and washing a Precipitate        |                       |

### (A) PRELIMINARY TESTS (DRY TESTS)

**1. STATE :- Solid, Liquid, Semi Liquid**

**2. COLOR :-**

No.	Color	Present
1.	Red	Pb <sub>3</sub> O <sub>4</sub> , As <sub>2</sub> S <sub>3</sub> , HgO, HgI <sub>2</sub> , Sb <sub>2</sub> S <sub>3</sub> , CrO <sub>3</sub> , Cu <sub>2</sub> O
2.	Orange-red	Dichromate
3.	Reddish-purple	Permanganates
4.	Pink	Cobalt, hydrated salts of manganese
5.	Yellow	CdS, AS <sub>2</sub> S <sub>3</sub> , SnS <sub>2</sub> , PbI <sub>2</sub> , HgO, Chromates, Iron(III), Chloride & Nitrate
6.	Green	Cr <sub>2</sub> O <sub>3</sub> , Hg <sub>2</sub> I <sub>2</sub> , Cr(OH) <sub>2</sub> , Fe(II) salts, Ni salts, CrCl <sub>2</sub> ·6H <sub>2</sub> O, CuCl <sub>2</sub> ·2H <sub>2</sub> O, CuCO <sub>3</sub>
7.	Blue	Anhydrous cobalt salts, Hydrated Cu(II) salts
8.	Brown	PbO <sub>2</sub> , CdO, Fe <sub>3</sub> O <sub>4</sub> , Ag <sub>3</sub> AsO <sub>4</sub> , SnS, Fe <sub>2</sub> O <sub>3</sub> , Bi <sub>2</sub> S <sub>3</sub>
9.	Reddish-brown	Fe(OH) <sub>3</sub>
10.	Orange	Sb <sub>2</sub> S <sub>3</sub>
11.	Black	PbS, CuS, CuO, HgS, FeS, MnO <sub>2</sub> , Co <sub>3</sub> O <sub>4</sub> , CoS, NiS, Ni <sub>2</sub> O <sub>3</sub> , Ag <sub>2</sub> S
12.	Gray	W, Mo, V, Zr, U
13.	Grayish-white	Mg, Be, Ti, Th, Ce
14.	Silver-white	Li

**3. SOLUBILITY :-**

The color of the solution obtained when the substance is dissolved in water or diluted acids should be noted.

1.	Blue	Copper (II) or Ni (for Sol. + DMG-Red ppt.)
2.	Green	Nickel, Iron(II), Chromium(III), Mangnates
3.	Yellow	Chromates, Hexacyanoferrate, Iron(II), (If CrO <sub>4</sub> <sup>-2</sup> present then K <sup>+</sup> must present)

4.	Orange-red	Dichromate (Sol. + AgNO <sub>3</sub> -Red ppt.-CrO <sub>4</sub> <sup>2-</sup> present)
5.	Purple	Permanganates
6.	Pink	Cobalt, Manganese(II)

#### 4. HEATING IN DRY TEST TUBE :-

Place a small quantity of the substance in a dry test-tube, heat cautiously

<b>(a)</b> The substance changes color		
1.	Blackening, not accompanied by burning or odor	Cu, Mn, Ni salts at very high temp.
2.	Orange when hot, white when cold	ZnO, & many Zn salts
3.	Brown when hot, yellow when cold	SnO <sub>2</sub> or Bi <sub>2</sub> S <sub>3</sub>
4.	Yellow when hot, yellow when cold	PbO & some Pb salts
5.	Brown when hot, red when cold	CdO & many Cd salts
6.	Red to black when hot, brown when cold	Fe <sub>2</sub> O <sub>3</sub>
<b>(b)</b> A sublimate is formed		
1.	White sublimate	Hg <sub>2</sub> Cl <sub>2</sub> , HgCl <sub>2</sub> , ammonium halides, Sb <sub>2</sub> O <sub>3</sub> etc.
2.	Gray sublimate	Hg
3.	Steel-gray sublimate	As
4.	Yellow sublimate	S, As <sub>2</sub> S <sub>3</sub> , HgI <sub>2</sub>
5.	Black- blue sublimate violet vapor	I
6.	Black-red on triturating	HgS
<b>(c)</b> A gas or vapour is evolved		
1.	Water is evolved	Compound with water, acid salts, ammonium Salts
2.	Dark brown or reddish fumes	Nitrates
3.	CO <sub>2</sub> is evolved (lime water rendered turbid)	Carbonates
4.	Ammonia is evolved (red litmus paper blue, mercury nitrate paper black)	Ammonium salts
5.	Phosphine is evolved (odor of fish)	Phosphates
6.	Sulphur dioxide is evolved (K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> paper green)	Sulphates, sulphites
7.	Hydrogen sulphide is evolved (lead acetate paper black,)	Sulphides
8.	Chloride is evolved (yellowish –green gas, bleaches litmus paper, turns potassium iodide starch paper blue)	Chloride
9.	Bromine is evolved (reddish brown vapour )	Bromides
10.	Iodine is evolved (violate vapour)	Iodides

#### 5. BLOWPIPE TESTS ON CHARCOAL :-

Heat a small portion of the material on charcoal in the **Oxidizing flame (O.F.)**, using a blowpipe. Scoop out a round hole in the charcoal, place a little of the substance in the cavity, and direct the inner flame of the blowpipe against it at an angle of thirty degrees.

Result of Test	Inference
Melts and runs into the charcoal	Alkalis. K, Na, etc.
An alkaline residue on charcoal	Ca, Sr, Ba, Mg
A residue which, when moistened with a drop of Co(NO <sub>3</sub> ) <sub>2</sub> and heated in <b>O. F.</b>	
(1) produces a color which is blue	Aluminum, silicon

(2) produces a color which is green	Zinc, tin, antimony
(3) produces a color which is red	Barium
(4) produces a color which is pink or rose-red	Manganese
Deflagrates	Nitrates, chlorates
Leaves an incrustation which is white near the flame	Antimony
White, garlic odor	Arsenic
Dark red	Silver
Red to orange	Cadmium
Lemon yellow (hot), light yellow (cold)	Lead
Orange yellow (hot), light yellow (cold)	Bismuth
Yellow (hot), white (cold)	Zinc or tin, later nonvolatile

### 5. (a) Blowpipe Tests (Substance fused with $\text{Na}_2\text{CO}_3$ on charcoal) :-

Place a small amount of the substance on charcoal with a little Sodium carbonate, and fuse, using **Reducing flame (R.F.)**

Result of Test	Inference
Metallic globules, without incrustation	
(1) Yellow flakes	Gold
(2) Red flakes	Copper
(3) White globule, moderately soft	Silver
Metallic globules, with incrustation	
(1) White, moderately soft beads	Lead or tin (volatilized lead leaves yellow coat)
(2) White, brittle beads	Bismuth or antimony (yellowish)
Yellow in <b>O. F.</b>	Chromium
Green in <b>O. F.</b>	Manganese
A substance (in <b>R. F.</b> ) which, when moistened and placed on a silver coin, leaves a brown or black stain	Sulfur compounds
Dark gray magnetic powder which, when moistened on a filter paper with a drop of dilute HCl and $\text{HNO}_3$ , and gently dried over a flame, leaves a stain which is faint	
pink, turning blue	Cobalt
Green stain, turning yellow	Nickel
A stain turned blue by $\text{K}_4[\text{Fe}(\text{CN})_6]$	Iron

### 5. (B) Blowpipe Test with Cobalt Nitrate :-

Substance moistened with cobalt nitrate solution and ignited.

Color of Residue or Incrustation	Inference
Brick red	$\text{BaO}$
Pink	$\text{MgO}$
Gray	$\text{SrO}$
Yellowish green	$\text{CaO}$
Dark muddy green	$\text{ZnO}$
Bluish green	$\text{Sb}_2\text{O}_5$
Blue	$\text{Al}_2\text{O}_3, \text{SiO}_2$

## 6. FLAME TEST :-

The platinum wire should be cleaned before making the test. This can be accomplished by dipping it into Con. HCl and holding it in the Bunsen, or, better, a flame of the blast lamp, until the flame is no longer colored. Repeated dipping into the HCl may be necessary.

Moisten a platinum wire in concentrated HCl, dip into the powdered substance and insert into a Bunsen flame. If sodium is prominent, examine through a blue glass. (Test the cobalt glass to see if it is effective in cutting out the yellow sodium light by examining a sodium flame through it.)

Examine the flame through a spectroscope, if available, and compare the spectra with a spectra chart. Mere traces of the alkali and alkaline earth metals can be detected in this way by either characteristic spectral lines.

Flame Color	Color through Blue Glass	Element
Carmine red	Purple	Lithium
Dull red	Olive green	Calcium
Crimson	Purple	Strontium
Golden yellow	Absorbed	Sodium
Greenish yellow	Bluish green	Barium, molybdenum
Green		Cu, -PO <sub>4</sub> , -B <sub>2</sub> O <sub>3</sub> ,
Blue		Cu, Bi, Pb, Cd, Zn, Sb, As
Violet	Violet red	Potassium

## 7. BEHAVIOR OF SUBSTANCES FUSED WITH BORAX BEADS AND MICROCOSMIC SALT, SODIUM AMMONIUM HYDROGEN PHOSPHATE :-

A clear bead is formed by fusing the flux on a loop of platinum wire. Dip the bead in the finely powdered substance to be examined, and heat again—first in the oxidizing flame; second in the reducing or inner flame. Metallic salts are mostly changed to oxides.

(a) With Sodium Tetraborate (Borax)				
Oxidizing Flame		Reducing Flame		Metal
Hot	Cold	Hot	Cold	
Green	Blue	Colorless	Opaque red or brown	Copper
Yellowish-brown	Yellow	Green	Green	Iron
Yellow	Green	Green	Green	Chromium
Violet (amethyst)	Amethyst	Colorless	Colorless	Manganese
Blue	Blue	Blue	Blue	Cobalt
Violet	Reddish-brown	Grey	Grey	Nickel
Yellow	Colorless	Brown	Brown	Molybdenum
Rose-violet	Rose-violet	Red	Violet	Gold
Yellow	Colorless	Yellow	Yellow-brown	Tungsten
Yellow	Pale yellow	Green	Bottle-green	Uranium

Yellow	Greenish-yellow	Brownish	Emerald-green	Vanadium
Yellow	Colorless	Grey	Pale-violet	Titanium
Orange-red	Colorless	Colorless	Colorless	Cerium
<b>(b) with Microcosmic salt, Sodium Ammonium Hydrogen Phosphate</b>				
<b>In the Table — <i>h.</i> signifies hot; <i>c.</i> cold; <i>sup.</i>, supersaturated with oxide; <i>s. s.</i>, strongly saturated; <i>h. c.</i>, hot and cold.</b>				
<b>Color of the bead</b>	<b>With Microcosmic Salt, Sodium Ammonium Hydrogen Phosphate</b>			
	<b>In outer or Oxidizing flame</b>		<b>In inner or reducing flame</b>	
Colorless	<b>Si</b> (swims undissolved). <b>Al, Mg, Ca, Sr, Ba, Sn</b> ( <i>s. s.</i> , opaque). <b>Ti, Zn, Cd, Pb, Ei, Sb</b> (not sat.).		<b>Si</b> (swims undissolved). <b>Al, Mg, Ca, Sr, Ba</b> ( <i>sup.</i> not clear) <b>Ce, Mn, Sn.</b>	
Yellow or Brownish	<i>h.</i> ( <i>s. s.</i> ): <b>Fe, U, Ce.</b> <i>c.</i> : <b>Ni.</b>		<i>h.</i> : <b>Fe, Ti.</b> <i>c.</i> : <b>Ni.</b>	
Red	<i>h.</i> ( <i>s. s.</i> ): <b>Fe, Ni, Cr, Ce.</b>		<i>c.</i> : <b>Cu</b> <i>h.</i> : <b>Ni, Ti with Fe.</b>	
Violet or Amethyst	<i>h. c.</i> : <b>Mn.</b>		<i>c.</i> : <b>Ti.</b>	
Blue	<i>h. c.</i> : <b>Co.</b> <i>c.</i> : <b>Cu.</b>		<i>h. c.</i> : <b>Co.</b> <i>c.</i> : <b>W.</b>	
Green	<i>h.</i> : <b>Cu, Mo; Fe</b> with <b>Co</b> or <b>Cu.</b> <i>c.</i> : <b>Cr.</b>		<i>c.</i> : <b>Cr.</b> <i>h.</i> : <b>U, Mo.</b>	
Gray and Opaque			<b>Ag, Pb, Sb, Cd, Bi, Zn, Ni.</b>	

## 8. TEST FOR AMMONIUM IONS:-

Sub. + NaOH (Heat)	The evolution of the ammonia, detected by its colour, red litmus paper turns blue & con. HCl glass rod gives white fumes of NH <sub>4</sub> Cl	NH <sub>4</sub> <sup>+</sup>
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## 9. TEST IN WATER EXTRACT:-

Take sub. In a boiling test tube and dilute with distilled water and boil it.

1.	Sol. + dill. HCl	Orange color solution after passing H <sub>2</sub> S turn green	CrO <sub>4</sub> <sup>-2</sup>
2.	Sol. + Nessler's reagent	Brown ppt	NH <sub>4</sub> <sup>+</sup>
3.	Sol. + Sodium Cobalti Nitrite	Yellow ppt	K <sup>+</sup>
4.	Sol. + Potassium pyro antimonate	White ppt	Na <sup>+</sup>
5.	<b>Ring test</b> Sol. + fresh FeSO <sub>4</sub> Sol. + Con. H <sub>2</sub> SO <sub>4</sub> By side of test tube	Brown ring between Layer	NO <sub>3</sub> <sup>-</sup>
		Solution becomes brown	NO <sub>2</sub> <sup>-</sup>

**For test of K<sup>+</sup>,** remove the NH<sub>4</sub><sup>+</sup> first, boil with NaOH and add dill. CH<sub>3</sub>COOH to neutralize of excess NaOH and then do the K<sup>+</sup> test.

After adding FeSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> the ppt if occur then possibility of Pb<sup>+2</sup>, Ba<sup>+2</sup>, Sr<sup>+2</sup>

## 10. REACTION OF THE ANIONS :-

Anions cannot be divided into groups in the same systematic way that the cations (metals) are divided. The process of examination for anions is, however, divided into the following two parts...

**A.** Identification by volatile products obtained on treatment with acids.

**B.** Identification by reactions in solution.

Each of these processes may again be subdivided according to the following reactions...

- a. (i) Gases evolved with dilute sulphuric acid.
- (ii) Gases, or volatile acid vapour, evolved with concentrated sulphuric acid.
- b. (i) Oxidation or reduction in solution.
- (ii) Precipitation.

1. Sub. + Dil. HCl	(a) Colorless gas is evolved with effervescence gas is odorless, make lime water milky (b) Reddish brown color & turning Starch iodide paper brown-black (c) The colorless gas is evolved with suffocating Odor, turns filter paper moistened with acidified $K_2Cr_2O_7$ solution green (d) Colorless gas is evolved, odor of rotten eggs, turns lead acetate paper black	$CO_3^{-2}$ $NO_2^-$ $SO_3^{-2}$ $S^{-2}$
2. Sub. + $MnO_2$ + Con. $H_2SO_4$	(a) Colorless gas evolved with pungent odor & white fumes of $NH_4Cl$ in contact with glass rod with con. $NH_3$ sol., turns litmus paper colorless (b) Reddish gas evolved with pungent odor, Turn starch paper yellow (Orange red) (c) Brownish gas which does not effect starch paper. (d) Violet vapor evolve accompanied by pungent acid fumes turn starch paper blue	$Cl^-$ $Br^-$ $NO_3^-$ $I^-$
3. Sub. + Cu foil + Con. $H_2SO_4$ (Heat)	Brown gas evolved	$NO_3^-$ $NO_2^-$
4. Phosphate test a). Sub. + Con. $HNO_3$ + ammo. molyb. Sol. (heat) b). Aqua. Sol. + ammo. moly. reagent large excess	Yellow ppt Yellow ppt	$PO_4^{-3}$ , $ASO_4^{-3}$ $PO_4^{-3}$
5. Sub. + drop Con. $H_2SO_4$ + Ethanol ignite alcohol	Burn with green flame	$BO_3^{-3}$

## 11. TEST WITH Conc. HCl :-

Heat about 0.5 gm powder with con. HCl and test follows.

Experiment	Observation	Interfance
1. Sol. + Con. HNO <sub>3</sub> , boil & add KCNS	Blood red coloration	Fe <sup>+2</sup> or Fe <sup>+3</sup>
2. Sol. + KCNS	Blood red coloration	Fe <sup>+3</sup>
3. Sol. + con. HNO <sub>3</sub> , Ammo. Moly. (in excess) & pass H <sub>2</sub> S	Crystalline yellow ppt	PO <sub>4</sub> <sup>-3</sup> or AsO <sub>4</sub> <sup>-3</sup>
4. Dilute the original sol., warm and pass H <sub>2</sub> S	Immediate yellow ppt Soluble in yellow (NH <sub>4</sub> ) <sub>2</sub> S	AsO <sub>3</sub> <sup>-3</sup>
5. Sol. + SO <sub>2</sub> water (Excess) boil off SO <sub>2</sub> & pass H <sub>2</sub> S	Yellow ppt, soluble In yellow (NH <sub>4</sub> ) <sub>2</sub> S	AsO <sub>3</sub> <sup>-3</sup>
6. Sol. SO <sub>2</sub> water, boil off excess of SO <sub>2</sub> pass H <sub>2</sub> S & filter, Add Con. HNO <sub>3</sub> & Ammo. Moly. to filtrate	Yellow ppt	PO <sub>4</sub> <sup>-3</sup>

## 12. GENERAL SUMMARY OF TESTS FOR ACIDS

Acids	Detecting Reagents	Reactions Resulting from Test
Acetates	H <sub>2</sub> SO <sub>4</sub> (con.)	Odor of vinegar
Arsenates	(a) (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> + HNO <sub>3</sub>	Yellow precipitate
	(b) Magnesia mixture	White granular precipitate
	(c) Reduced on C + Na <sub>2</sub> CO <sub>3</sub>	Garlic odor, arsenic mirror
Arsenites	(a) Magnesia mixture	No reaction
	(b) H <sub>2</sub> S + HCl	Yellow precipitate
Bromides	(a) H <sub>2</sub> SO <sub>4</sub> (con.)	Red Br vapor
	(b) Chlorine water + CS <sub>2</sub>	Reddish color, due to Br
Borates	H <sub>2</sub> SO <sub>4</sub> (con.) + alcohol + Burn	Green flame
Carbonates	Dilute acids	CO <sub>2</sub> evolved. Limewater test
Chlorates	(a) H <sub>2</sub> SO <sub>4</sub> (con.)	Explosive liberation of Cl + ClO <sub>2</sub>
	(b) Heated alone	O given off
Chlorides	AgNO <sub>3</sub> + HNO <sub>3</sub>	White precipitate, sol. in NH <sub>4</sub> OH
Chromates	(a) H <sub>2</sub> SO <sub>4</sub> (con.)	O liberated (sol. yellow to green)
	(b) HCl	Chlorine of HCl liberated
Cyanides	(a) Alcohol + NaOH	Reduced and Cr(OH) <sub>3</sub> precipitated
	H <sub>2</sub> SO <sub>4</sub> (con.)	HCN (POISON). Odor, bitter almonds
Ferricyanides	FeSO <sub>4</sub> + HCl	Turnbull's blue precipitate
Ferrocyanides	FeCl <sub>3</sub> + HCl	Prussian blue precipitate
Fluorides	H <sub>2</sub> SO <sub>4</sub> (con.)	HF gas liberates silicic acid from glass rod with drop of H <sub>2</sub> O
Hypochlorites	Dilute acids	Cl liberated, yellow gas
Iodides	(a) H <sub>2</sub> SO <sub>4</sub> (con.)	Violet vapor of iodine
	(b) Chlorine water + CS <sub>2</sub>	Violet color to CS <sub>2</sub>
Nitrates	FeSO <sub>4</sub> + H <sub>2</sub> SO <sub>4</sub> (con.)	Brown ring
Nitrites *	Dilute acids	N <sub>2</sub> O <sub>3</sub> brown evolved
Oxalates	H <sub>2</sub> SO <sub>4</sub> (con.)	CO + CO <sub>2</sub> evolved
Permanganates	Reducing agents	Decolorized
Phosphates	HNO <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> at 40°	Yellow precipitate
Silicates	(a) Fused with Na <sub>2</sub> CO <sub>3</sub> and HCl Added	Silicic acid precipitated

	(b) HF	SiF <sub>4</sub> gas liberated
Sulfates	HCl + BaCl <sub>2</sub>	White precipitate of BaSO <sub>4</sub>
Sulfides	Dilute acids	H <sub>2</sub> S gas blackens Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>
Sulfites	Dilute acids	SO <sub>2</sub> gas
Sulfocyanides	FeCl <sub>3</sub>	Deep red color
Thiosulfates	Dilute acids	SO <sub>2</sub> gas + free S
Tartrates	Ignited	Char. Odor of burnt sugar
Organic acids	Heated	Generally char

\* Nitrites + KI + CS<sub>2</sub> = violet color in CS<sub>2</sub> due to free I<sub>2</sub>.

### TABLE SHOWING GROUP REAGENTS AND RADICALS

Group	Group reagent	Group radical	Salt ppts
<b>I</b>	Dil. HCl	Ag, Hg, Pb, W, Tl	As chloride & H <sub>2</sub> WO <sub>4</sub>
<b>II</b>	Dil HCl + H <sub>2</sub> S gas	Pt, Au, Hg, As, Se, Te, Mo, Pb, Bi, Cu, Pd, Sn, Sb, Cd	As sulphides in acidic medium
<b>III – A</b>	Remove H <sub>2</sub> S by boiling + NH <sub>4</sub> Cl + NH <sub>3</sub>	Fe, Cr, Al, Ti, Zr, Ce, Th, V, U	As hydroxide
<b>III – B</b>	3-A centrifugate + H <sub>2</sub> S gas	Co, Ni, Mn, Zn	As sulphide in alkaline medium
<b>IV</b>	Remove H <sub>2</sub> S by boiling + NH <sub>4</sub> Cl + NH <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	Ba, Ca, Sr	As carbonates
<b>V</b>	4 <sup>th</sup> centrifugate + NH <sub>4</sub> Cl + NH <sub>4</sub> OH + Na <sub>2</sub> HPO <sub>4</sub>	Mg	As phosphates

## SEPARATION AND IDENTIFICATION OF CATIONS INTO GROUPS

### Separation of Group I:

#### Separation and identification of Group I cations in the presence of TI and W

The precipitate may contain  $\text{PbCl}_2$ ,  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{TlCl}$ , and tungstic acid ( $\text{WO}_3 \cdot x\text{H}_2\text{O}$ ). Wash the precipitate on the filter with 2 ml portions of 2M HCl, then 2-3 times with 1 ml portions of cold water, and reject the washings. Transfer the precipitate<sup>a</sup> to a boiling tube or to a small beaker, and boil with 10-15 ml water. Filter hot.

(TABLE I)

Residue		Filtrate		
May contain $\text{Hg}_2\text{Cl}_2$ , $\text{AgCl}$ , and tungstic acid. Wash the ppt. several times with hot water until the washings give no ppt. with 0.1 M $\text{K}_2\text{CrO}_4$ solution; this ensures the complete removal of the Pb and Tl. Pour 5 ml warm, 2M $\text{NH}_3$ solution repeatedly through the filter.		May contain $\text{Pb}^{2+}$ and $\text{Tl}^+$ ; these may crystallize out on cooling. Evaporate to fuming with 2-3 ml Concentrated $\text{H}_2\text{SO}_4$ , cool, dilute to 10-20 ml, cool and filter.		
Residue	Filtrate	Residue	Filtrate	
If black, consists of $\text{Hg}(\text{NH}_2)\text{Cl} + \text{HgHg(I)}$ present.	May contain $\text{Ag}(\text{NH}_3)_2^+$ and $\text{WO}_4^{2-}$ . Nearly neutralize with 2M HCl, add just enough 2M $\text{NH}_3$ solution to re-dissolve any ppt. which forms. Add 0.1M KI solution and filter. <sup>b</sup>	If white - consists of $\text{PbSO}_4$ . This is Soluble in 6M Ammonium Acetate solution; $\text{K}_2\text{CrO}_4$ Solution then precipitates yellow $\text{PbCrO}_4$ , insoluble in 2M acetic acid. <b>Pb present.</b>	May contain $\text{Tl}^+$ Just neutralize with 2M $\text{NH}_3$ solution, and add 0.1M KI solution. Yellow ppt. of Tl, insoluble in cold 0.5M $\text{Na}_2\text{S}_2\text{O}_3$ solution. <b>Tl present.</b> Confirm by flame test; intense green flame. (Use spectroscope, if available.)	
	<table border="1"> <thead> <tr> <th>Residue</th> <th>Filtrate</th> </tr> </thead> <tbody> <tr> <td>Pale yellow (AgI). <b>Ag present.</b></td> <td>May contain <math>\text{WO}_4^{2-}</math>. Evaporate to a small volume, acidify with 2M HCl, add 3 ml, 0.25 M <math>\text{SnCl}_2</math> solution, boil, add 3 ml concentrated HCl, and heat again to boiling. <b>Blue ppt. or coloration.</b> <b>W present.</b> Confirm by the Defacqz reaction</td> </tr> </tbody> </table>			Residue
Residue	Filtrate			
Pale yellow (AgI). <b>Ag present.</b>	May contain $\text{WO}_4^{2-}$ . Evaporate to a small volume, acidify with 2M HCl, add 3 ml, 0.25 M $\text{SnCl}_2$ solution, boil, add 3 ml concentrated HCl, and heat again to boiling. <b>Blue ppt. or coloration.</b> <b>W present.</b> Confirm by the Defacqz reaction			

<sup>a</sup> A gelatinous precipitate may also be hydrated silica, which is partially precipitated here from silicates decomposed by acids.

<sup>b</sup> The solution obtained after dissolving in ammonia should be discarded quickly to avoid a serious **Explosion !**

### Confirmative tests for group – I

#### (1) Hg (Mercury)

Aq.sol. + dil.HCl → white ppt. of  $\text{Hg}_2\text{Cl}_2$  insoluble in dil. acids

Aq.sol. +  $\text{H}_2\text{S}$  in neutral or dil.acid medium → black ppt.of Hgs.

Aq.sol. +  $\text{NH}_3$  sol. → black ppt. (which itself is a white ppt.)

Aq.sol. + NaOH → black ppt of  $\text{Hg}_2\text{O}$ . insoluble in excess reagent, dissolve in dil.  $\text{HNO}_3$

Aq.sol. +  $\text{K}_2\text{CrO}_4$  in hot sol. → red ppt. (test in cold, brown ppt)

Aq.sol. + KI added slowly in cold sol. → green ppt of  $\text{Hg}_2\text{I}_2$ .

Aq.sol. +  $\text{Na}_2\text{CO}_3$  → yellow ppt of  $\text{Hg}_2\text{CO}_3$ , it turns slowly in blackish grey.

Aq.sol. +  $\text{Na}_2\text{HPO}_4$  → white ppt of  $\text{Hg}_2\text{HPO}_4$

**(2) Ag (silver)**

- Aq.sol. + dil HCl → white ppt of AgCl dissolve in con HCl  
 Aq.sol. + H<sub>2</sub>S in neutral acidic medium → black ppt of Ag<sub>2</sub>S  
 Aq.sol. + NH<sub>3</sub> sol. → brown ppt of Ag<sub>2</sub>O and dissolve in excess of reagent  
 Aq.sol. + NaOH → brown ppt of Ag<sub>2</sub>O. The ppt dissolves in excess of reagent  
 Aq.sol. + KI → yellow ppt of AgI is insoluble in dil. or con NH<sub>3</sub>  
 Aq.sol. + K<sub>2</sub>CrO<sub>4</sub> → red ppt of Ag<sub>2</sub>CrO<sub>4</sub>  
 Aq.sol. + Na<sub>2</sub>CO<sub>3</sub> → yellowish white ppt of Ag<sub>2</sub>CO<sub>3</sub>  
 Aq.sol. + Na<sub>2</sub>HPO<sub>4</sub> → yellow ppt of Ag<sub>3</sub>PO<sub>4</sub> dissolve in HNO<sub>3</sub> & NH<sub>3</sub> sol.

**(3) Pb (lead)**

- Aq.sol. + dil HCl → white ppt of PbCl<sub>2</sub> soluble in hot water & con HCl  
 Aq.sol. + H<sub>2</sub>S in neutral acidic medium → black ppt of PbS  
 Aq.sol. + NH<sub>3</sub> sol. → white ppt of Pb(OH)<sub>2</sub> insoluble in excess of reagent  
 Aq.sol. + NaOH → white ppt of Pb(OH)<sub>2</sub> soluble in excess of reagent [Pb(OH)<sub>4</sub>]<sup>-2</sup>  
 Aq.sol. + KI → yellow ppt of PbI<sub>2</sub> is moderately soluble in boiling water  
 Aq.sol. + K<sub>2</sub>CrO<sub>4</sub> → yellow ppt of PbCrO<sub>4</sub>, dissolve in HNO<sub>3</sub>  
 Aq.sol. + Na<sub>2</sub>SO<sub>3</sub> in neutral sol. → white ppt of PbSO<sub>3</sub>  
 Aq.sol. + Na<sub>2</sub>HPO<sub>4</sub> → white ppt of Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> soluble in NaOH/ strong acid  
 Aq.sol. + Dithiozone → Red color complex

**(4) W (Tungsten)**

- Aq.sol. + dil HCl → white ppt of H<sub>2</sub>WO<sub>4</sub> · H<sub>2</sub>O in cold  
 Aq.sol. + phosphoric acid → white ppt of phosphor tungstic acid soluble in excess of reagent  
 Aq.sol. + (NH<sub>4</sub>)<sub>2</sub>S sol. → brown ppt. of WS<sub>3</sub>, dissolves in excess  
 Aq.sol. + HCl & little Zn → blue ppt or coloration is produced  
 Aq.sol. + SnCl<sub>2</sub> sol. → yellow ppt which becomes blue upon warming with con HCl.  
 Aq.sol. + FeSO<sub>4</sub> sol. → brown ppt which turns white upon adding dil. HCl  
 Aq.sol. + AgNO<sub>3</sub> sol. → pale yellow ppt. soluble in NH<sub>3</sub> Sol.

**(5) Tl (Thallium):-**

- Aq.Sol. + dil HCl → white ppt. of TlCl sparingly soluble in cold, more soluble in hot water  
 Aq.Sol. + KI soln. → yellow ppt. Tl, insoluble in water, insoluble in sodium thiosulphate  
 Aq.Sol. + K<sub>2</sub>CrO<sub>4</sub> → yellow ppt. of Tl<sub>2</sub>CrO<sub>4</sub> insoluble in cold, dil. HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>.  
 Aq.Sol. + ammonium sulphide sol. → black ppt soluble in mineral acids  
 Aq.Sol. + sodium hexanitritocobaltate(III) sol. → light red ppt of Tl<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>]  
 Aq. sol. + ammoniumthiocyanate sol. → white ppt dissolve in hot H<sub>2</sub>O  
 Aq sol. + NaOH or NH<sub>3</sub> sol. → brown ppt on soluble in excess of reagent, soluble in HCl

**Separation of Group – II**

**Separation of Group II cations into Groups IIA and IIB in the presence of Mo, Au, Pt, Pd, Se, and Te**

The precipitate may consist of the sulphides of the Group **II A** metals (HgS, PbS, Bi<sub>2</sub>S<sub>3</sub>, CuS, CdS) and those of Group **II B** (As<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>5</sub>, SnS, SnS<sub>2</sub>). Transfer the Group **II** precipitate, which has been well washed with NH<sub>4</sub>Cl solution that has been saturated with H<sub>2</sub>S, to a porcelain dish, add 5-10ml ammonium polysulphide solution, heat to 50- 60°C and maintain at this temperature for 3-4 minutes with constant stirring. Filter. Wash the precipitate with dilute ammonium polysulphide solution.

**(TABLE II)**

<b>Residue</b>	<b>Filtrate</b>
May contain HgS, PbS, Bi <sub>2</sub> S <sub>3</sub> , CuS, CdS, PdS Together with Au, Pt, traces Of MoS <sub>3</sub> and SnS.  <b>II A present.</b>	May contain solutions of the thio salts (NH <sub>4</sub> ) <sub>3</sub> AsS <sub>4</sub> , (NH <sub>4</sub> ) <sub>2</sub> SbS <sub>4</sub> , and (NH <sub>4</sub> ) <sub>2</sub> SnS <sub>3</sub> , together with Mo, Au, Pt, Se, and Te. Just acidify by adding concentrated HCl drop wise (test with litmus paper), and warm gently. A colored precipitate indicates  <b>II B present.</b>

For the separation of cations in to Groups **II A and II B** the procedure of Table **II** should be followed. The separation and identification of Group **II A** cations can be carried out by following the procedures given in Table **III**, and **II B** by Table **IV**

### **Separation of Group II A**

#### **Separation and Identification of Group II A cations in the presence of Pt, Au, and Pd.**

The precipitate may contain sulphides of the group II A HgS, PbS, Bi<sub>2</sub>S<sub>3</sub>, CuS, CdS, and PdS, together with Au and Pt and also traces of MoS<sub>3</sub> and SnS. Transfer to a beaker or porcelain dish, add 5-10 ml 2M HNO<sub>3</sub>, boil for 2-5 minutes and filter and wash with a little water.

(TABLE III)

Residue		Filtrate	
May contain Pb, Bi, Cu, Cd, and Pd ions. Examine for Pb, Bi, Cu, and Cd After separation of Cu and Cd, Dived into two parts			
May contain HgS, Pt, and Au. Boil with concentrated HCl and a little bromine water, and filter,if necessary, from traces of SnO <sub>2</sub> and PbSO <sub>4</sub> which separate here. Add KCl solution and 2M HCl, and concentrate the solution. Filter.		(1) Test a small portion for Pb by adding Dilute H <sub>2</sub> SO <sub>4</sub> and alcohol. A white ppt. of PbSO <sub>4</sub> indicates <b>Pb present</b> . If Pb present, Add H <sub>2</sub> SO <sub>4</sub> to the remainder of the solution, concentrate in the fume cupboard until white fumes (from the decomposition of the H <sub>2</sub> SO <sub>4</sub> ) appear. Cool, add 10 ml of water, stir, allow to stand 2-3 minutes, filter and wash with a little water.	(2) Acidify the solution with HCl, introduce a few Zinc granules and after several minutes filter any ppt. solid and filter with water. Dissolve the ppt. in 2 ml aqua regia, evaporate just to dryness, dissolve the residue in 2M HCl and add dimethylglyoxime reagent. Yellow ppt. <b>Pd Present</b>
Residue	Filtrate	Residue	Filtrate
Yellow and Crystalline K <sub>2</sub> [PtCl <sub>6</sub> ] <b>Pt present.</b>	May contain [AuCl <sub>2</sub> ] and HgCl <sub>2</sub> Boil to remove excess acid, render alkaline with 2M NaOH solution, and boil with excess 0.5M oxalic acid. Filter.	White: PbSO <sub>4</sub> .  Pour 2 ml of 3M ammonium acetate through the filter several times, add to the filtrate a few drops of 2M acetic acid and then 0.1M K <sub>2</sub> CrO <sub>4</sub> solution. Yellow ppt. of PbCrO <sub>4</sub> . <b>Pb present.</b>	May contain nitrates and sulphates of Bi, Cu and Cd. Add concentrated NH <sub>3</sub> solution until solution is distinctly alkaline. Filter.
	Residue		Filtrate
	Brownish-Black or Purpalish-Black. <b>Au present.</b>		White: may be Bi(OH) <sub>3</sub> . Wash. Dissolve in the minimum volume of 2M HCl and pour into cold sodium tetrahydroxotannate(II). Black ppt. <b>Bi present.</b> Alternatively; dissolve a little 2-3 drops 2M HNO <sub>3</sub> . Place 1 drop of this solution upon filter paper moistened with cinchonine-KI reagent. Orange-red spot. <b>Bi present.</b>
	May contain HgCl <sub>2</sub> . Add a few drops of 0.25M SnCl <sub>2</sub> sol.'n White or gray ppt. <b>Hg present.</b>		May contain [Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>+2</sup> and [Cd(NH <sub>3</sub> ) <sub>4</sub> ] <sup>+2</sup> If deep blue color, Cu is present in quantity. Confirm Cu by acidifying a portion of the filtrate with 2M acetic acid And add K <sub>4</sub> [Fe(CN) <sub>6</sub> ] solution. Reddish-brown ppt. <b>Cu present.</b> To the remainder of the filtrate ,add KCN solution dropwise until color is discharged, and add a further ml in excess. Pass H <sub>2</sub> S for 20-30 seconds. Yellow ppt., sometimes discoloured, of CdS. <b>Cd present.</b> Filter off ppt. and dissolve a portion of it in 1 ml 2M HCl boil to expel H <sub>2</sub> S and most of the acid and apply the "cation-2B' test on 1 drop of the solution. A pink spot <b>confirms Cd.</b>

## Confirmative tests for group – II A

### 1. Pt (Platinum)

Aq.sol. +  $H_2S$  → black or brown ppt. of  $PtS_2$  insoluble in con. Acids, dissolve in aqua regia

Aq.sol. + KCl sol. → yellow ppt from con sol. A similar result are obtain with  $NH_4Cl$

Aq.sol. +  $AgNO_3$  sol. → yellow ppt soluble in  $NH_3$  solution

Aq.sol. +  $SnCl_2$  → red or yellow coloration soluble in ethyl acetate or ether

Aq.sol. + Rubinic acid → purple red ppt of complex.

Dry test : All Pt- compounds when fused with  $Na_2CO_3$  upon charcoal are reduced

### 2. Au (gold):-

Aq.sol. +  $H_2S$  → black ppt of  $Au_2S$  in the cold, insoluble in dil. acids, soluble in  $(NH_4)_2S$

Aq.sol. +  $NH_3$  sol. → yellow ppt of fulminating gold.

Aq.sol. + oxalic acid sol. → brown powder ppt from cold neutral sol.

Aq.sol. +  $SnCl_2$  → purple ppt if the sol. Is con. HCl dark brown ppt

Aq.sol. +  $H_2O_2$  → the finally divided metal is ppt. in the presence of NaOH sol.

Aq.sol. + NaOH → reddish-brown ppt from con.soln.dissolves in excess alkali.

### 3. Bi(Bismuth):-

Aq.sol. +  $H_2S$  → black ppt insoluble in cold, dil. acid and in ammo. sulphide

Aq.sol. +  $NH_3$  sol. → white basic salt, insoluble in excess reagent

Aq.sol. + NaOH – white ppt of  $Bi(OH)_3$  in excess of reagent very slightly soluble

Aq.sol. + KI when added drop wise → black dissolve readily in excess reagent.

Aq.sol + water → white ppt of the corresponding salt, soluble in dil. Mineral acids basis

Aq.sol + pyrogallol (10%), when added slightly excess to a hot, faintly acid sol of Bi-ion → yellow ppt.

Aq.sol. + thiourea (10%) → yellow ppts. In the presence of dil  $HNO_3$ .

Aq.sol. + 8-Hydroxyquinoline (5%) and potassium iodide in acidic medium → red ppt.

### 4. Pd(Palladium):-

Aq.sol. +  $H_2S$  → black ppt from acid or neutral soln. insoluble in ammonium sulphide

Aq.sol. +  $NH_3$  sol. → redish-brown ppt gelatinous ppt soluble in excess of the reagent

Aq.sol. + NaOH → white ppt of  $Pd(OH)_2$  insoluble in excess of reagent.

Aq.sol. + KI soln. → black ppt. in neutral soln. soluble in excess of the reagent to give a brown soln. in acid, black.

Aq.sol. + DMG → yellow ppt, insoluble in dil. HCl, soluble in dil.  $NH_3$

### 5. Cu(Copper) :-

Aq.sol. +  $H_2S$  → black ppt in acid medium

Aq.sol. +  $NH_3$  sol. → blue ppt of a basic salt.

Aq.sol. + NaOH sol. In cold → blue ppt.

Aq.sol. + KI → white ppt. but soln. is brown

Aq.sol. + Potassium thiocyanate → black ppt. decomposes slowly

Aq.sol. +  $\alpha$ -benzoinoxime (cupron) → green ppt in 5% alcohol

Aq.sol. + Rubeanic acid → black ppt. in ammonical or dil. acid solution

Aq.sol. + Salicylaldoxime → greenish-yellow ppt in acetic acid

## 6. Pb (Lead)

Aq.sol. + dil HCl → white ppt, soluble in hot water & con. HCl

Aq.sol. + H<sub>2</sub>S → black ppt, in neutral or dilute acid medium

Aq.sol. + NH<sub>3</sub> sol → white ppt, insoluble in excess of reagent

Aq.sol. + NaOH → white ppt, soluble in excess of reagent [Pb(OH)<sub>4</sub>]<sup>-2</sup>

Aq.sol. + KI → yellow ppt, moderately soluble in boiling water

Aq.sol. + K<sub>2</sub>CrO<sub>4</sub> → yellow ppt, dissolve in NaOH and HNO<sub>3</sub>

Aq.sol. + Na<sub>2</sub>SO<sub>3</sub> → white ppt, in neutral sol.

Aq.sol. + Na<sub>2</sub>HPO<sub>4</sub> → white ppt, soluble in HNO<sub>3</sub> and NaOH

Aq.sol. + Dithiozone → red color complex

## 7. Cd (Cadmium):-

Aq.sol. + H<sub>2</sub>S → yellow ppt

Aq.sol. + NH<sub>3</sub> sol. When added dropwise → white ppt

Aq.sol. + NaOH soln. → white ppt

Aq.sol. + KCN → white ppt. soluble in excess reagent

## 8. Hg (Mercury)

Aq.sol. + H<sub>2</sub>S → first white and finally black ppt in the presence of dil HCl

Aq.sol. + NH<sub>3</sub> sol. → white mixed ppt of Hg(II) oxide and mercury(II) amidonitrate

Aq.sol. + NaOH sol. → yellow ppt, insoluble in excess reagent, dissolve in acids

Aq.sol. + KI → red ppt. dissolves in excess reagent

Aq.sol. + SnCl<sub>2</sub> → white ppt of Hg<sub>2</sub>Cl<sub>2</sub>

## Separation of Group – II B

### Separation and identification of Group IIB cations in the presence of Pt, Au, Se, Te, and Mo

Transfer the precipitate to a small conical flask, add 5 ml concentrated HCl, and boil gently for 5 minutes (with funnel in mouth of flask). Dilute with 2-3 ml water and filter.

(TABLE IV)

Residue	Filtrate		
May contain As, Au, Pt, Mo, Se, and Te as sulphides. Dissolve in concentrated HCl + little solid $KClO_3$ , concentrate the solution to the crystallization point (use a water bath to reduce loss of <b>Se</b> to a minimum). Filter.	May contain Sb and Sn as chlorides or complex chloro-acids. Boil to expel $H_2S$ , and divide the cold solution into three parts. (1) Render just alkaline with 2M $NH_3$ solution, disregard any slight ppt., add 1-2 g solid oxalic acid, boil, and pass $H_2S$ for 1 minute into the hot filtrate. Orange ppt. of $Sb_2S_3$ . <b>Sb present.</b> (2) To 2 drops of the solution on a spot plate, add a minute crystal of $NaNO_2$ and then 2 drops of Rhodamine-B reagent. Violet solution or ppt. <b>Sb present.</b> (3) Partially neutralize the liquid with 2M $NH_3$ , add 10 cm clean iron wire to 1 ml of the solution. (If much Sb is present, it is better to reduce with Mg powder.) Warm gently to reduce the tin to the divalent state, and filter into a solution of $HgCl_2$ . White ppt. of $Hg_2Cl_2$ or grey ppt. of Hg. <b>Sn present.</b>		
Residue	Filtrate		
Yellow $K_2[PtCl_6]$ . <b>Pt present.</b> Conform by dissolving in a little hot water and adding 0.1M KI solution. Red or brownish-red coloration.	May contain As, Au, Mo, Se, and Te as chlorides or acids. Render alkaline with 2M $NH_3$ solution, add $Mg(NO_3)_2$ reagent or magnesia mixture, allow to stand for 5 minutes with frequent stirring or shaking. Filter.		
Residue	Filtrate		
White Crystalline $Mg(NH_3) \cdot AsO_4 \cdot 6H_2O$ . <b>As Present.</b>	May contain Au, Mo, Se, and Te as chlorides or acids. Concentrate to remove ammonia, boil with several milliliters saturated oxalic acid solution, dilute, boil and filter. Extract ppt. with 2M HCl to remove coprecipitated tellurous acid.		
	Residue	Filtrate	
	Brownish-black or purplish-black. <b>Au present.</b>	Concentrate with 6M HCl on a water bath and, after removing the precipitated KCl, treat with a slight excess of solid $Na_2SO_3$ . Filter.	
	Red <b>Se present.</b>	Residue	Filtrate
		Black. <b>Te present.</b>	Dilute with an equal volume of water, and add successively a little 0.1M KI solution and excess of solid $Na_2SO_3$ where by the $[Te_6]^{-2}$ ions are reduced to Te. Filter. Boil with 2M HCl to remove dissolved $SO_2$ and treat successively with 10% KSCN soln and a little 0.25M $SnCl_2$ soln. Red coloration, soluble in ether. <b>Mo present.</b>

### Confirmative tests for group – II B

#### 1. As(Arsenic)

Aq.sol. +  $H_2S$  → yellow ppt insoluble in con. HCl.,

Aq.sol + Copper sulphate soln. → green ppt. from neutral soln. soluble in acids and also in  $NH_3$

Aq.sol. + potassium triiodide(soln. of iodine in KI) oxidizing as ion while becoming decolorized.

Aq.sol. +  $SnCl_2$  and con. HCl → A few drops of As-soln. + 2ml con HCl & 0.5 saturat  $SnCl_2$  soln. warmed, dark brown soln. and black.

Aq.sol. + ammonium molybdate soln. → when reagent and  $HNO_3$  added in excess to a soln. of As yellow crystal ppt. is obtained on boiling, insoluble in  $HNO_3$ .

#### 2. Se(Selenium)

Aq.sol. +  $H_2S$  → yellow ppt in the cold, becoming red on heating, soluble in ammonium sulphide

Aq.sol + BaCl<sub>2</sub> sol. → white ppt in neutral soln. soluble in dil. Acid

Aq.sol. + Copper sulphate soln. → bluish-green ppt in neutral soln. soluble in dil. CH<sub>3</sub>COOH

Aq.sol. + Thiourea → red powder of Se

Aq.sol. + NH<sub>4</sub>SCN → red coloration as selenites are reduce to Se

Aq.sol. + KI + HCl → reddish-brown power of Se remains, as selenites are reduce

### 3. Te(Tellurium):-

Aq.sol. + H<sub>2</sub>S → brown ppt from acid soln. soluble in ammonium sulphide soln.

Aq.sol. + BaCl<sub>2</sub> sol. → white ppt in neutral soln. soluble in dil. acid

Aq. Sol. + KI soln. → yellow to red color from dil. acid soln.

Aq.sol + SO<sub>2</sub> → complete ppt. from dil. HCl as a black powder, In the presence of much con. HCl

Aq.sol. + SnCl<sub>2</sub> or hydrogen soln. or Zinc → Black ppt hydrochloride

Aq.sol. + dil HCl → white ppt., soluble in excess of the precipitant.

### 4. Mo(Molybdenum):-

Aq.sol. + H<sub>2</sub>S → blue coloration with acidified soln.

Aq.sol. + ammonium thiocyanate sol. → yellow coloration in soln. acidify dill. HCl, becoming blood red, with Zn or SnCl<sub>2</sub>

Aq.sol. + Na<sub>2</sub>HPO<sub>4</sub> → yellow ppt in the presence of exces HNO<sub>3</sub>

Aq.sol. + K<sub>4</sub>[Fe(CN)<sub>6</sub>] → reddish-brown ppt, soluble in KOH and NH<sub>3</sub>

Aq.sol. + α-benzoinoxime(cupron) → white ppt. with strongly acidified with dil. H<sub>2</sub>SO<sub>4</sub> Soln.

Aq.sol. + Phenylhydrazine → red coloration or ppt. is produced in acidic medium

Aq.sol. + Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> → reddish brown color, upon addition mineral acid

### 5. Sb(Antimony):-

Aq.sol. + H<sub>2</sub>S → orange-red ppt. soluble in warm con. HCl and in alkali hydroxide soln.

Aq.sol + water → sol. is poured into H<sub>2</sub>O white ppt. soluble in HCl.

Aq.sol + NaOH or NH<sub>3</sub> sol. → white ppt. soluble in con. soln. of caustic alkali

Aq.sol. + KI → yellow coloration

Aq.sol. + Rhodamine – B → violet or blue coloration with quinquevalent antimony

Aq.sol. + Zn or Sn → black ppt. of Sb in the presence of HCl.

### 6. Sn(Tin):-

Aq.sol. + H<sub>2</sub>S → brown ppt. soluble in con. HCl also soluble in (NH<sub>4</sub>)<sub>2</sub>S soln..

Aq.sol. + NaOH sol. → white ppt. soluble in excess alkali with NH<sub>3</sub> soln.

Aq.sol. + Hg<sub>2</sub>Cl<sub>2</sub> → white ppt. if a large reagent is added due to Sn(II) ions excess, gray ppt.

Aq.sol. + Bismuth nitrate and NaOH soln. → black ppt. due to Bi Metal

Borax bead test → A borax bead which has been colored pale-blue.

## REMOVAL OF PHOSPHATE

### (a) Iron (III) Acetate Method

If a phosphate has been found proceed as follows. Dissolve the precipitate produced by the action of NH<sub>4</sub>Cl and a slight excess of NH<sub>3</sub> solution in the minimum volume of 2M HCl. [The precipitate may contain Fe(OH)<sub>3</sub>, Al(OH)<sub>3</sub>, Cr(OH)<sub>3</sub>, MnO<sub>2</sub>·xH<sub>2</sub>O, traces of CaF<sub>2</sub>, and the phosphates of Mg and the Group IHA, IIB, and IV metals.] Test

about 0.5ml for Fe by the addition of  $K_4[Fe(CN)_6]$  or 0.1M  $NH_4SCN$  solution. To the main volume of the cold solution, add 2M  $NH_3$  solution drop wise, with stirring, until either a faint permanent precipitate is just obtained or until the solution is just alkaline (test with litmus paper). Then add 2-3 ml 9M acetic acid and 5 ml 6M ammonium acetate solution. Disregard any precipitate which may form at this stage. If the solution is red or brownish-red, sufficient iron(III) is present in the solution to combine with all the phosphate ions. If the solution is not red in color, add almost neutral  $FeCl_3$  solution drop by drop and with stirring, until the solution acquires a deep brownish-red color. Dilute the solution to about 150 ml with hot water, boil gently for 1-2 minutes, filter hot and wash the residue with a little boiling water.

**(B) Zirconium Nitrate Method**

Reduce the solution (filtrate of group 2) about 10 ml, by evaporation if necessary. Adjust the con. HCl so that it does not exceed. Add solution of  $NH_4Cl$ , stir until dissolve, add zirconium nitrate slowly and with stirring until precipitation is completed. Heat the content just to boiling and stir, with glass rod to prevent boiling. Filter it. Wash the ppt. With hot water and combine the washing with filtrate.

**(C) Tin (Iv) Chloride Method**

Boil the filtrate from group-2 to remove  $H_2S$ , add  $(NH_4)_2HPO_4$  solution (if necessary) followed by dilute  $NH_3$  solution until the ppt which formed initially does not redissolved on shaking. Add dil. HCl heat to boiling and introduce 2 ml of  $SnCl_4$  reagent. Filter 1-2 ml the suspension and test the filtrate for phosphate with ammonium molybdate and  $HNO_3$  if the test is positive than further add  $SnCl_4$  to boiling suspension repeat the process until  $PO_4^{-3}$  is negligible and filter the boiling suspension, wash with hot  $H_2O$ .

**Separation of Group – III A**

**Separation and identification of Group IIIA cations in the presence of Ti, Zr, Ce, Th, U, and V.**

Dissolve the precipitate in the minimum volume of 2M HCl. Pour the weakly acid solution into an equal volume of a solution which contains 2 ml 30%  $H_2O_2$  and is 2.5M with respect to NaOH. (The latter solution should be freshly prepared.) Boil for 5 minutes, but no longer. Filter and wash the precipitate with hot 2%  $NH_4NO_3$  solution.

(TABLE V)

Residue	Filtrate	
May contain $\text{Fe}(\text{OH})_3$ ; $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ ; $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ ; $\text{ThO}_2 \cdot x\text{H}_2\text{O}$ ; $\text{CeO}_3 \cdot x\text{H}_2\text{O}$ (and some $\text{MnO}(\text{OH})_2$ ).  Dissolve in 2M HCl, boil to expel $\text{Cl}_2$ and divide the solution into five parts. <b>(1)</b> Add 0.1 M KSCN solution. Red coloration. <b>Fe present.</b> <b>(2)</b> If Fe present, add just sufficient $\text{H}_3\text{PO}_4$ to mask iron(III) ions, and then 3% $\text{H}_2\text{O}_2$ . Orange- red coloration, discharged by the addition of solid $\text{NH}_4\text{F}$ . <b>Ti present.</b> White ppt. <b>Zr present.</b> <b>(3)</b> Add excess saturated oxalic acid solution. White ppt. <b>Th and/or Ce present.</b> <b>(4)</b> separation of <b>Th</b> and <b>Ce</b> They may be separated from the other metals of the group by dissolving the precipitate in 2MHCl and adding oxalic acid solution, when the oxalates of both metals are precipitated. The <b>Th</b> and <b>Ce</b> may be separated: (a) by dissolving the thorium oxalate in a mixture of ammonium acetate solution and acetic acid, cerium oxalate being insoluble under these conditions; (b) by treatment with a large excess of hot con. ammonium oxalate solution; only the thorium oxalate dissolves (a complex ion being formed), and may be reprecipitated from the resultant solution as oxalate by the addition of hydrochloric acid. <b>(5)</b> Evaporate to fuming with 8M $\text{H}_2\text{SO}_4$ to expel HCl. Cool, dilute, add 2M $\text{HNO}_3$ and a little $\text{NaBiO}_3$ . Stir and stand. Purple colouration. <b>Mn present.</b>	May contain $\text{CrO}_4^{-2}$ , $[\text{Al}(\text{OH})_4]^-$ , $\text{VO}_3^-$ , and $\text{U}_2\text{O}_7^{-2}$ Acidify with 2M $\text{HNO}_3$ ; add 3-4ml 0.25M $\text{Pb}(\text{NO}_3)_2$ solution, followed by 2 g solid ammonium acetate. Stir well, filter and wash with hot water.	
	Residue	Filtrate
	May contain $\text{PbCrO}_4$ and $\text{Pb}(\text{VO}_3)_2$ . Dissolve in the min. volume of hot 2M $\text{HNO}_3$ (~5-6ml), thoroughly cool the resulting solution, and transfer to a small separating funnel. Add an equal volume of amyl alcohol, and a little 3% $\text{H}_2\text{O}_2$ . Shake well and allow the two layers to separate. A blue coloration in the upper layer indicates <b>Cr present,</b> and a red to brownish- red coloration in the lower layer indicates <b>V present.</b> Confirm <b>V</b> by the $\text{KClO}_3$ -p-phenetidine Test.	May contain $\text{Al}^{+3}$ , $\text{UO}_2^{+2}$ and excess of $\text{Pb}^{2+}$ . Pass $\text{H}_2\text{S}$ to remove all the Pb as $\text{PbS}$ . Filter, wash and boil the filtrate to expel $\text{H}_2\text{S}$ . Almost neutralize with 2M $\text{NH}_3$ solution, cool and pour in to an excess of concentrated $(\text{NH}_4)_2\text{CO}_3$ solution. Warm For 5 min. Allow to stand, filter and wash.
	Residue	Filtrate
	White: $\text{Al}(\text{OH})_3$ . <b>Al present.</b> Confirm by Thenard's blue test.	May contain U, probably as $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ Evaporate to a Small volume, acidify with 2M HCl and add $\text{K}_4\text{Fe}(\text{CN})_6$ solution. Brown ppt. of $(\text{UO}_2)_2[\text{Fe}(\text{CN})_6]$ becoming yellow upon the addition of 2M NaOH solution. <b>U present.</b>

### Confirmative tests for group – III A

#### (1) Fe (Iron)

aq. Soln. + NaOH Soln. → white ppt, insoluble in excess but soluble in acids.

aq. Soln. +  $\text{NH}_3$  soln. → white ppt. of iron-2 hydroxide, soluble in acids.

Aq. Soln. +  $(\text{NH}_4)_2\text{S}$  → black ppt. readily soluble in acids with evolution of  $\text{H}_2\text{S}$

Aq. Soln. +  $\text{K}_4[\text{Fe}(\text{CN})_6]$  → pale blue ppt. of  $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ , potassium iron(II) hexacyanoferrate(II)

Aq. Soln. +  $[\text{Fe}(\text{CN})_6]$  → dark blue ppt. of  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (Turnbull's blue)

#### (2) Ti(Titanium):-

aq. Soln. + alkalis → white gelations ppt, in the cold. Soluble in mineral acids.

aq. Soln. +  $\text{H}_2\text{O}$  → a white ppt. acid is obtained on boiling a soln. (metatitanic)

Aq. Soln. +  $\text{Na}_2\text{HPO}_4$  soln. → white ppt. in dilute  $\text{H}_2\text{SO}_4$  soln.

Aq. Soln. + Cupferron reagent → yellow ppt. in acid soln.

Aq. Soln. +  $\text{H}_2\text{O}_2$  → Orange-red coloration in slightly acid soln. color is yellow white with very dilute soln.

Aq. Soln. + Pyrocatachol reagent → yellow coloration with neutral or weakly acid soln.

### (3) Th(Thorium):-

Aq. Soln. + Alkline reagent → white ppt. insoluble in excess reagent, soluble in dilute acids.

Aq. Soln. +  $\text{Na}_2\text{CO}_3$  soln. → white ppt. soluble in excess of reagent

Aq. Soln. + oxalic acid soln. → white ppt. insoluble in excess reagent

Aq. Soln. + Ammonium oxalate soln. → white ppt, dissolve of boiling with excess reagent

Aq. Soln. + saturated  $\text{K}_2\text{SO}_4$  soln. → white ppt. soluble in dil. HCl

Aq. Soln. +  $\text{H}_2\text{O}_2$  → white ppt soluble in dil. HCl.

Aq. Soln. +  $\text{K}_4[\text{Fe}(\text{CN})_6]$  → white ppt in neutral or acid soln.

Aq. Soln. + potassium iodate soln. → white ppt occurs in presence of 50% volume of con.  $\text{HNO}_3$

Aq. Soln. + m-nitro benzoic acid → addition of excess reagent to neutral soln. at 80 degree centigrade → white ppt.

### (4) Ce(Cerium):-

aq. Soln. +  $\text{NH}_3/\text{NaOH}$  → yellow ppt. of  $\text{Ce}(\text{OH})_4$ , Ce(III) ions formed on warming with HCl

aq. Soln. + oxalic acid or Ammonium oxalate soln. → white ppt., insoluble in excess reagent and dil. acids.

Aq. Soln. +  $\text{K}_2\text{SO}_4$  soln. → white ppt. in neutral and from slightly acid soln.

Aq. Soln. +  $\text{H}_2\text{O}_2$  → Ce salt treated with  $\text{NH}_3$  soln. excess  $\text{H}_2\text{O}_2$  added → yellowish-brown or reddish-brown ppt.

Aq. Soln. + sodium bismuth soln. → reagent in presence of dil.  $\text{HNO}_3$  in cold yellow-orange color

Aq. Soln. + potassium iodate soln. → white ppt in neutral soln. soluble in  $\text{HNO}_3$

Aq. Soln. + sodium thio sulphate soln. → yellow color of solution discharged.

### (5) Mn(Mangenesese):-

Aq. Soln. + NaOH → initially white ppt. insoluble in excess reagent.

Aq. Soln. +  $(\text{NH}_4)_2\text{S}$  soln. → pink ppt soluble mineral acids.

Aq. Soln. +  $\text{Na}_2\text{HPO}_4$  soln. → pink ppt of in the presence of ammonia.

Aq. Soln. +  $\text{PbO}_2$  + con.  $\text{HNO}_3$  → boiling Soln. free from Cl with  $\text{PbO}_2$  little con.  $\text{HNO}_3$  → violet-red color.

### (6) Cr(Chromium):-

aq. Sol. +  $\text{NH}_3$  soln. → grey-green to blue gelatinous ppt. slightly soluble in excess in cold forming violet or pink.

Aq. Sol. + NaOH sol. → ppt. of  $\text{Cr}(\text{OH})_3$ , on addition of acids and excess reagent ppt dissolves

Aq. Sol. +  $\text{Na}_2\text{CO}_3/(\text{NH}_4)_2\text{S}$  → ppt of chromium hydroxide.

Aq. Sol. +  $\text{Na}_2\text{HPO}_4$  soln. → green ppt. soluble in mineral acids, insoluble in cold dil. acetic acid.

### (7) V(Vandadium):-

aq. Sol. +  $\text{H}_2\text{S}$  → Blue soln. is formed and sulphur separates.

Aq. Sol. + Zn, Cd or Al in acid soln. → the soln. turns at first blue then green and finally violet.

Aq. Sol. +  $(\text{NH}_4)_2\text{S}$  → red colored soln. on acidification brown ppt.

Aq. Sol. +  $\text{H}_2\text{O}_2 \rightarrow$  a red coloration is produced.

Aq. Sol. +  $\text{NH}_4\text{Cl} \rightarrow$  soln. of an alkali in results colorless crystallize, ammonium vanadate soluble in con.  $\text{NH}_4\text{Cl}$ .

Aq. Sol. + Lead acetate  $\rightarrow$  yellow ppt. soluble in dil.  $\text{HNO}_3$

Aq. Sol. + Copper sulphate  $\rightarrow$  green or yellow ppt.

Aq. Sol. + mercury nitrate soln.  $\rightarrow$  white ppt. from neutral soln.

### (8) Al(Aluminium):-

aq. Sol. +  $\text{NH}_3$  sol.  $\rightarrow$  white gelatinious ppt. slightly soluble in excess reagent.

Aq. Sol. +  $\text{NaOH} \rightarrow$  white ppt dissolve in excess reagent

Aq. Sol. +  $(\text{NH}_4)_2\text{S}$  soln.  $\rightarrow$  white ppt dissolve in excess reagent

Aq. Sol. +  $\text{Na}_2\text{HPO}_4$  soln.  $\rightarrow$  white ppt dissolve in strong acids, insoluble in  $\text{CH}_3\text{COOH}$

Aq. Sol. + Aluminon  $\rightarrow$  bright-red absorption on aluminium hydroxide

Aq. Sol. + alizarin  $\rightarrow$  red lake with aluminium hydroxide

### (9) U(Uranium):-

Aq. Sol. +  $\text{H}_2\text{S} \rightarrow$  black ppt from acid or neutral soln. insoluble in ammonium sulphide.

Aq. Sol. +  $\text{NH}_3 \rightarrow$  yellow ppt., insoluble excess of reagent, soluble in  $(\text{NH}_4)_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$ .

Aq. Sol. +  $\text{NaOH} \rightarrow$  yellow ppt, soluble in  $(\text{NH}_4)_2\text{CO}_3$ .

Aq. Sol. +  $(\text{NH}_4)_2\text{S} \rightarrow$  brown ppt. soluble in dil. Acids and in  $(\text{NH}_4)_2\text{CO}_3$  soln.

Aq. Sol. +  $\text{Na}_2\text{HPO}_4$  soln.  $\rightarrow$  white ppt, soluble mineral acids, insoluble in dil. Acetic acid.

Aq. Sol. + ammonium or sodium carbonate  $\rightarrow$  white ppt soluble excess reagent.

Aq. Sol. +  $\text{K}_4[\text{Fe}(\text{CN})_6]$  soln.  $\rightarrow$  brown ppt. in neutral or acetic acid, soluble in dil.  $\text{HCl}$

### (10) Zr(Zirconium):-

Aq. Sol. +  $\text{NaOH} \rightarrow$  white gelatinous ppt, soluble in dil. mineral acid

Aq. Sol. +  $\text{NH}_3$  /  $(\text{NH}_4)_2\text{S} \rightarrow$  white gelatinous ppt of hydroxides

Aq. Sol. +  $\text{H}_2\text{O}_2 \rightarrow$  white ppt. in slightly acidic soln.

Aq. Sol. +  $\text{NaHPO}_4$  soln.  $\rightarrow$  white gelatinous ppt. of hydroxides

Aq. Sol. +  $(\text{NH}_4)_2\text{CO}_3 \rightarrow$  white ppt soluble in excess and reprecipitated on boiling

Aq. Sol. +  $\text{H}_2\text{C}_2\text{O}_4$  soln.  $\rightarrow$  white ppt. Soluble in excess of reagent

Aq. Sol. +  $\text{K}_2\text{C}_2\text{O}_4$  soln.  $\rightarrow$  white ppt. insoluble in excess of reagent

Aq. Sol. +  $\text{KIO}_3$  soln.  $\rightarrow$  white ppt. in faintly acid soln.

Aq. Sol. + Alizarin red S  $\rightarrow$  red ppt. in strongly acid medium

## SEPARATION OF GROUP – III B

The precipitate may contain  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{MnS}$  and  $\text{ZnS}$ . Wash well with 1%  $\text{NH}_4\text{Cl}$  solution to which 1% by volume of  $(\text{NH}_4)_2\text{S}$  has been added; reject the washings. Transfer the precipitate to a small beaker. Add 5 ml water and 5 ml 2M  $\text{HCl}$ , stir well, allow to stand for 2-3 minutes and filter.

**(TABLE VI)**

<b>Residue</b>	<b>Filtrate</b>	
If black, may contain CoS and NiS. Test residue with borax bead. If blue, Co is indicated. Dissolve the ppt. in a mixture of 1.5ml M NaOCl and 0.5ml 2M HCl. Add 1 ml 2M HCl, and boil until all Cl <sub>2</sub> is expelled. Cool and dilute to about 4 ml. Divide the solution into two equal parts. Add 1 ml amyl alcohol, 2 g solid NH <sub>4</sub> SCN and shake well. Amyl alcohol layer colored blue. <b>Co present.</b> Add 2 ml NH <sub>4</sub> Cl M solution, 2M NH <sub>3</sub> solution until alkaline, and then excess of dimethylglyoxime reagent. Red ppt. <b>Ni present.</b>	May contain Mn <sup>2+</sup> and Zn <sup>2+</sup> and, possibly, traces of Co <sup>2+</sup> and Ni <sup>2+</sup> . Boil until H <sub>2</sub> S removed (test with lead acetate paper), cool, add excess 2M NaOH solution, followed by 1 ml 3% H <sub>2</sub> O <sub>2</sub> solution. Boil for 3 minutes. Filter.	
	<b>Residue</b>	<b>Filtrate</b>
Largely MnO(OH) <sub>2</sub> and perhaps traces of Ni(OH) <sub>2</sub> and Co(OH) <sub>3</sub> . Dissolve the ppt. in 5 ml of 8M HNO <sub>3</sub> , with the addition of a few drops of 3% H <sub>2</sub> O <sub>2</sub> solution, if necessary. Boil to decompose excess H <sub>2</sub> O <sub>2</sub> and cool. Add 0.05g NaBiO <sub>3</sub> , stir and allow to settle. Purple solution of MnO <sub>4</sub> <sup>-</sup> <b>Mn present.</b>	May contain [Zn(OH) <sub>4</sub> ] <sup>-2</sup> Divide into two parts. (1) Acidify with 2M acetic acid and pass H <sub>2</sub> S. White ppt. of ZnS. <b>Zn present.</b> (2) Just acidify with H <sub>2</sub> SO <sub>4</sub> , add 0.5ml of 0.1M cobalt acetate solution and 0.5 ml of the ammonium tetrathiocyanato-mercurate(II) reagent: stir. Pale blue ppt. <b>Zn present.</b>	

**Confirmative tests for group – III B****(1) Co(Cobalt)**

- Aq. Sol. + NaOH → blue salt. Which upon warming with alkali, pink ppt  
 Aq. Sol. + (NH<sub>4</sub>)<sub>2</sub>S soln → black ppt, insoluble in dil. HCl or CH<sub>3</sub>COOH, dissolve in aqua regia  
 Aq. Sol. + KNO<sub>2</sub> soln → yellow ppt. of K<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>]·3H<sub>2</sub>O, in the presence of CH<sub>3</sub>COOH  
 Aq. Sol. + NH<sub>4</sub>SCN → blue color of [Co(SCN)<sub>4</sub>]<sup>-2</sup>  
 Aq. Sol. + 1-nitroso-2-naphthol → redish-brown ppt. of Co(C<sub>10</sub>H<sub>6</sub>O<sub>2</sub>N)<sub>3</sub>

**(2) Ni(Nickel)**

- Aq. Sol. + NaOH → green ppt. of Ni(OH)<sub>2</sub> dissolve in ammonia.  
 Aq. Sol. + NH<sub>3</sub> soln. → green ppt. of Ni(OH)<sub>2</sub> dissolve in excess reagent  
 Aq. Sol. + (NH<sub>4</sub>)<sub>2</sub>S soln → black ppt. from neutral or alkali soln.  
 Aq. Sol. + potassium nitrate soln. → no ppt. produced in presence of acetic acid  
 Aq. Sol. + DMG reagent → red ppt from alkaline with NH<sub>3</sub>  
 Aq. Sol. + Rubeanic acid → blue or violet ppt or coloration in ammonical soln.

**(3) Zn(Zinc)**

- Aq. Sol. + NaOH → white gelatinious ppt. soluble in acids and excess reagent  
 Aq. Sol. + NH<sub>3</sub> soln → white ppt. really soluble in excess reagent  
 Aq. Sol. + (NH<sub>4</sub>)<sub>2</sub>S soln → white ppt. dissolves in dil. mineral acid  
 Aq. Sol. + Na<sub>2</sub>HPO<sub>4</sub> soln. → white ppt soluble in dil. acids.  
 Aq. Sol. + K<sub>4</sub>[Fe(CN)<sub>6</sub>] soln → white ppt if reagent is added in slightly excess

**(4) Mn(Manganese)**

- Aq. Sol. + NaOH → white ppt. of Mn(OH)<sub>2</sub>, insoluble in excess reagent  
 Aq. Sol. + NH<sub>3</sub> soln → white ppt. of Mn(OH)<sub>2</sub>, really soluble in excess reagent  
 Aq. Sol. + (NH<sub>4</sub>)<sub>2</sub>S soln → black ppt. of MnS dissolves in dil. mineral acid  
 Aq. Sol. + Na<sub>2</sub>HPO<sub>4</sub> soln. → pink ppt. of Mn(NH<sub>4</sub>)PO<sub>4</sub>

**SEPARATION OF GROUP IV CATIONS**

The precipitate may contain  $\text{BaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CaCO}_3$ . Wash with a little hot water and reject the washings. Dissolve the precipitate in 5 ml hot 2M acetic acid by pouring the acid repeatedly through the filter paper. Test 1 ml for barium by adding 0.1M  $\text{K}_2\text{CrO}_4$  solution dropwise to the nearly boiling solution. A yellow precipitate indicates Ba.

**Ba present.**

Heat the remain solution almost to boiling and add a slight excess of 0.1M  $\text{K}_2\text{CrO}_4$  solution (i.e. until the solution assumes a yellow color and precipitation is complete). Filter and wash the precipitate (C) with a little hot water. Render the hot filtrate and washings basic with 2M  $\text{NH}_3$  solution and add excess M  $(\text{NH}_4)_2\text{CO}_3$  solution or, better, a little solid  $\text{Na}_2\text{CO}_3$ . A white precipitate indicates the presence of  $\text{SrCO}_3$  and/or  $\text{CaCO}_3$ . Wash the precipitate with hot water, and dissolve it in 4 ml warm 2M acetic acid: boil to remove excess  $\text{CO}_2$  (solution A).

**Ba absent.**

Discard the portion used in testing for barium, and employ the remainder of the solution (B), after boiling for 1 minute to expel  $\text{CO}_2$ , to test for strontium and calcium.

(TABLE VII)

Residue (C)	Solution (A) or (B)	
Yellow: $\text{BaCrO}_4$ Wash well with hot water. Dissolve the ppt. in a little concentrated HCl, evaporate almost to dryness and apply the flame test. Green (or yellowish-green) flame.  <b>Ba present.</b> (Use spectroscope, if available.)	The volume should be about 4 ml. Either - To 2 ml of the cold solution, add 2 ml saturated $(\text{NH}_4)_2\text{SO}_4$ solution, followed by 0.2 g sodium thiosulphate, heat in a beaker of boiling water for 5 minutes and allow to stand for 1 -2 minutes. Filter. Or - To 2 ml of the solution add 2 ml triethanolamine, 2 ml saturated $(\text{NH}_4)_2\text{SO}_4$ solution, heat on a boiling water bath with continuous stirring for 5 minutes and allow to stand for 1-2 minutes. Dilute with an equal volume of water and filter.	
	Residue	Filtrate
	Largely $\text{SrSO}_4$ . Wash with a little water. Transfer ppt. and filter to a small crucible, heat until ppt. has charred (or burn filter paper and ppt., held in a Pt wire, over a crucible), moisten ash with a few drops concentrated HCl and apply the flame test. Crimson flame. <b>Sr present.</b> (Use spectroscope, if available.)	May contain Ca complex. (If Sr is absent, use 2 ml of solution A or B.) Add a little 0.1M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution, 2ml 2M $\text{CH}_3\text{COOH}$ and warm on a water bath. White ppt. of $\text{CaC}_2\text{O}_4$ . <b>Ca present.</b> Confirm by flame test on ppt. -- brick-red flame. (Use spectroscope, if available.)

**Confermative tests for group – IV**

(1) **Ba(Barium)**

Aq. Sol. +  $(\text{NH}_4)_2\text{CO}_3 \rightarrow$  white ppt soluble in acetic acid and dil. mineral acids.

Aq. Sol. +  $(\text{COONH}_4)_2$  soln.  $\rightarrow$  white ppt redily dissolve by hot dil. acetic acid

Aq. Sol. + dil.  $\text{H}_2\text{SO}_4 \rightarrow$  white ppt, insoluble in water and dill. Acids.

Aq. Sol. +  $\text{CaSO}_4 \rightarrow$  white ppt of  $\text{BaSO}_4$

Aq. Sol. +  $\text{K}_2\text{CrO}_4 \rightarrow$  yellow ppt insoluble in water and dil. acetic acid.

Aq. Sol. + sodium rhodizonate  $\rightarrow$  reddish brown ppt in neutral soln.

(2) **Sr(Strontium)**

Aq. Sol. +  $(\text{NH}_4)_2\text{CO}_3 \rightarrow$  white ppt. of  $\text{SrCO}_3$

Aq. Sol. +  $\text{H}_2\text{SO}_4 \rightarrow$  white ppt. of  $\text{SrSO}_4$ , insoluble in  $(\text{NH}_4)_2\text{SO}_4$ .

Aq. Sol. +  $\text{CaSO}_4 \rightarrow$  white ppt of  $\text{SrSO}_4$

Aq. Sol. +  $\text{K}_2\text{CrO}_4 \rightarrow$  yellow ppt. of  $\text{SrCrO}_4$ , soluble in  $\text{CH}_3\text{COOH}$  and in mineral acids

Aq. Sol. + sodium rhodizonate → brown ppt.

### (3) Ca(Calcium)

Aq. Sol. +  $(\text{NH}_4)_2\text{CO}_3$  → white ppt. of  $\text{CaCO}_3$

Aq. Sol. +  $\text{H}_2\text{SO}_4$  → white ppt. of  $\text{CaSO}_4$ , dissolves in hot con.  $\text{H}_2\text{SO}_4$

Aq. Sol. +  $\text{K}_4[\text{Fe}(\text{CN})_6]$  → white ppt. of  $\text{K}_2\text{Ca}[\text{Fe}(\text{CN})_6]$

Aq. Sol. + sodium dihydroxytartrate → yellow sparingly-soluble ppt of the Ca salt

## Identification of Group V cations

Treat the dry residue from Group IV with 4 ml water, stir, warm for 1 minute and filter. If the residue dissolves completely (or almost completely) in water, dilute the resulting solution (after filtration, if necessary) to about 6 ml and divide it into three approximately equal parts: (1) use the major portion to test for Mg with the 2% 8-hydroxyquinoline solution: confirm Mg by applying the magneson test to 3-4 drops of the solution; (2) and (3) test for Na and K, respectively, as described below.

(TABLE VIII)

Residue	Filtrate
Dissolve in a few drops of 2M HCl and add 2-3 ml water. Divide the solution into two unequal parts. (1) Larger portion: Treat 1 ml 2% m 8-hydroxyquinoline solution in 2M acetic acid with 5 ml 2M ammonia solution and, if necessary, warm to dissolve any precipitated oxine. Add a little $\text{NH}_4\text{Cl}$ solution to the test solution, followed by the ammoniacal oxine reagent, and heat to boiling point for 1-2 minutes (the odor of $\text{NH}_3$ should be discernible). Pale yellow ppt. of Mg 'oxinate'. <b>Mg present.</b> (2) Smaller portion: To 3-4 drops, add 2 drops of the magneson reagent, followed by several drops of 2M NaOH solution until alkaline. A blue ppt. <b>confirms Mg.</b>	Divide into two parts (a) and (b). (a) Add a little uranyl magnesium acetate reagent, shake and allow to stand for a few Yellow crystalline ppt. <p style="text-align: center;"><b>Na present.</b></p> Confirm by flame test: persistent yellow flame. (b) Add a little sodium hexa nitrito cobaltate (III) solution (or 4mg of the solid) and a few drops of 2M acetic acid. Stir and, if necessary, allow to stand for 1-2 minutes. Yellow ppt. of $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ . <p style="text-align: center;"><b>K present.</b></p> Confirm by flame test and view through two thicknesses of Cobalt glass: red coloration (usually transient).

## Confermative tests for group – V

### (1) Mg(Magnesium)

Aq. Sol. +  $\text{NH}_3$  soln. → white gelatinous ppt. of  $\text{Mg}(\text{OH})_2$

Aq. Sol. + NaOH soln. → white ppt. of  $\text{Mg}(\text{OH})_2$

Aq. Sol. +  $(\text{NH}_4)_2\text{CO}_3$  → white ppt. of  $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$

Aq. Sol. +  $\text{Na}_2\text{HPO}_4$  soln → white ppt. in presence of  $\text{NH}_4\text{Cl}$  and ammonia soln. soluble in  $\text{H}_2\text{O}$

Aq. Sol. + 8-hydroxyquinoline → soln. of Mg-salt, little  $\text{NH}_4\text{Cl}$ , add  $\text{NH}_3$  → hit– yellow ppt.

Aq. Sol. + Titan yellow → deep-red ppt. with alkaline soln.

### (2) K (Potassium)

Aq. Soln. +  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$  soln. → yellow ppt. of  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ , insoluble in  $\text{CH}_3\text{COOH}$

Aq. Soln. + sodium hydrogen tartrate soln. → white crystallize ppt.

Aq. Soln. + HClO<sub>4</sub> soln. → white ppt, slightly soluble in water.

Aq. Soln. + Dipicrylamine → crystalline orange-red ppt.

Flame test → intense reddish-violet through cobalt glass

### (3) NH<sub>4</sub> (Ammonium ion)

Aq. Soln. + NaOH → ammonia gas is evolved on warming, white fumes with con. HCl glass rod.

Aq. Soln. + Nessler's reagent → brown ppt or brown or yellow coloration.

Aq. Soln. + Na<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] Sodium cobaltinitrite → yellow ppts. of (NH<sub>4</sub>)<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>]

Aq. Soln. + saturated sodium hydrogen tartrate soln. → white ppt. of NH<sub>4</sub>·H·C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>

### (4) Li (Lithium)

Aq. Soln. + Na<sub>2</sub>HPO<sub>4</sub> soln. → partial ppt. of Li<sub>3</sub>PO<sub>4</sub> in neutral soln.

Aq. Soln. + Na<sub>2</sub>CO<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> soln. → white ppt. of Li<sub>2</sub>CO<sub>3</sub>

Aq. Soln. + NH<sub>4</sub>F soln. → white gelatinous ppt is slowly formed in ammonical soln.

Flametest: Li compound impart a carmine-red color to the non-luminous burner flame.

### (5) Na(Sodium)

Aq. Soln. + uranile-Mg-acetate → yellow ppt. of NaMg(UO<sub>2</sub>)<sub>3</sub> (CH<sub>3</sub>COO)<sub>9</sub>·9H<sub>2</sub>O

Aq. Soln. + Tartaric acid → no ppt.

Aq. Soln. + uranile-Zn-acetate → yellow crystalline ppt. of NaZn(UO<sub>2</sub>)<sub>3</sub> (CH<sub>3</sub>COO)<sub>9</sub>·9H<sub>2</sub>O

Flame Test → intense yellow

## (C) Reaction of the anions

The method for the detection of anions is not as systematic as cations and they can not be divided into groups. However, for the easy detection of the anions, It can be divide into main two group depending upon process employed on them.

### 1. By volatile products obtained with acids

(A) Gases evolved with dilute sulphuric acid :- Carbonates, sulphites, sulphide, Nitrite

(B) Gases or volatile acid vapours, evolved with con. H<sub>2</sub>SO<sub>4</sub> :- Chloride, Bromide, Iodide, Nitrate, Borate

### 2. By reaction in solution

(A) Oxidation or reduction in solution :- Chromate, Dichromate

(B) Precipitation :- Sulphate, Phosphate, Arsenate, Chromate, Arsenite, Dichromate

#### (1) CO<sub>3</sub><sup>-2</sup> (Carbonate)

Aq. Soln. + dil. HCl → Decomposition with effervescence due to the evolution of CO<sub>2</sub>, limewater turbid.

Aq. Soln. + BaCl<sub>2</sub> or CaCl<sub>2</sub> soln. → white ppt, soluble in mineral acids.

Aq. Soln. + AgNO<sub>3</sub> soln. → White ppt, soluble in HNO<sub>3</sub> and in ammonia

Aq. Soln. + Na<sub>2</sub>CO<sub>3</sub> → phenolphthalein test → this test depends upon phenolphthalein is turn pink by soluble.

**(2)  $\text{SO}_3^{-2}$  (Sulphites):-**

- Aq. Soln. + dil. HCl or  $\text{H}_2\text{SO}_4$  → decomposition, more rapidly of warming with evolution of  $\text{SO}_2$
- Aq. Soln. +  $\text{BaCl}_2$  or  $\text{SnCl}_2$  sol. → white ppt., dissolve in dil. HCl.
- Aq. Soln. +  $\text{AgNO}_3$  soln. → first no changes addition more reagent gives white ppt.
- Aq. Soln. +  $\text{KMnO}_4$  soln. → acidify with dil  $\text{H}_2\text{SO}_4$  before the test decolorizing owing to reduction to manganese II ions
- Aq. Soln. + lead acetate  $\text{Pb}(\text{NO}_3)_2$  soln. → white ppt dissolve in dil.  $\text{HNO}_3$
- Aq. Soln. + Zn and  $\text{H}_2\text{SO}_4$  →  $\text{H}_2\text{S}$  gas is evolved. Lead acetate paper black

**(3)  $\text{S}^{-2}$  (sulphides):-**

- Aq. Soln. + dil HCl or dil.  $\text{H}_2\text{SO}_4$  →  $\text{H}_2\text{S}$  gas evolved. Lead acetate paper black
- Aq. Soln. +  $\text{AgNO}_3$  soln. → black ppt. soluble in hot dil.  $\text{HNO}_3$
- Aq. Soln. + lead acetate soln. → black ppt of lead sulphide
- Aq. Soln. + sodium nitropruside soln. → purple color in alkali soln.

**(4)  $\text{NO}_2^-$  (Nitrites):-**

- Aq. Soln. + dil. HCl → pale-blue liquid, evolution of brown fumes.
- Aq. Soln. +  $\text{FeSO}_4$  soln. +  $\text{H}_2\text{SO}_4$  → brown color solution
- Aq. Soln. +  $\text{AgNO}_2$  soln. → white ppt. from con. solution.
- Aq. Soln. + KI soln. →  $\text{NO}_2$  soln. to a KI soln., followed by acidify with  $\text{CH}_3\text{COOH}$  or dil.  $\text{H}_2\text{SO}_4$   
→ liberation of iodine.
- Aq. Soln. +  $\text{KMnO}_4$  soln. → acidify and decolorization due to reduction, but no gas evolved.
- Aq. Soln. + Urea → acidify with dil. HCl,  $\text{NO}_2$  decomposed,  $\text{N}_2$  and  $\text{CO}_2$  evolved.
- Aq. Soln. + Thiourea → when dil.  $\text{CH}_3\text{COOH}$  soln. of  $\text{NO}_2$  &  $\text{FeCl}_3$  are little thiourea,  $\text{N}_3$  is evolved, red color produce with dill. HCl.

**(5)  $\text{Cl}^-$  (Chlorides):-**

- Aq. Soln. + Con.  $\text{H}_2\text{SO}_4$  → decomposition of chloride in cold, on warming with evolution of HCl, pungent odor, white fumes with ammonia soln. blue litmus paper turns red.
- Aq. Soln. +  $\text{AgNO}_3$  soln. → white ppt, soluble in  $\text{NH}_3$  soln. and  $\text{Na}_2\text{S}_2\text{O}_3$  soln., insoluble in water.
- Aq. Soln. + lead acetate soln. → white ppt. from concentrated soln.
- Aq. Soln. +  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$  → chloride mixed with 3 times  $\text{K}_2\text{Cr}_2\text{O}_7$  powder, equal bulk con.  $\text{H}_2\text{SO}_4$  warmed – deep – red fumes.

**(6)  $\text{Br}^-$  (Bromides):-**

- Aq. Soln. + con.  $\text{H}_2\text{SO}_4$  → first reddish-brown soln. is formed, after reddish-brown vapour
- Aq. Soln. +  $\text{MnO}_2$  + Con.  $\text{H}_2\text{SO}_4$  → mixture is warmed, reddish-brown vapors, irritating odor, starch paper orange-red.
- Aq. Soln. + lead acetate soln. → white ppt., soluble in boiling water.
- Aq. Soln. +  $\text{AgNO}_3$  soln. → pale yellow ppt., sparingly soluble in dilute, readily soln. in con.  $\text{NH}_3$ .

**(7)  $\Gamma$  (Iodides):-**

Aq. Soln. + con.  $\text{H}_2\text{SO}_4 \rightarrow$  iodine is liberated on warming, violet vapor evolved, starch paper blue.

Aq. Soln. +  $\text{AgNO}_3$  soln.  $\rightarrow$  yellow ppt. of  $\text{AgI}$ , soluble in  $\text{Na}_2\text{S}_2\text{O}_3$

Aq. Soln. + lead acetate soln.  $\rightarrow$  yellow ppt. soluble in much hot water colorless soln. yellowish-golden plates on cool.

Aq. Soln. +  $\text{K}_2\text{Cr}_2\text{O}_7$  + con.  $\text{H}_2\text{SO}_4 \rightarrow$  iodine is liberates

Aq. Soln. +  $\text{CuSO}_4$  soln.  $\rightarrow$  brown ppt. of  $\text{CuI}$  and iodine.

Aq. Soln. +  $\text{HgCl}_2$  soln.  $\rightarrow$  Scarlet ppt. of  $\text{HgI}_2$ , dissolve in excess  $\text{KI}$ , forms  $[\text{HgI}_4]^{-2}$

**(8)  $\text{NO}_3^-$  (Nitrates)**

Aq. Soln. + con.  $\text{H}_2\text{SO}_4 \rightarrow$  reddish-brown vapour of nitrogen dioxide.

Aq. Soln. + con.  $\text{H}_2\text{SO}_4$  +  $\text{Cu}$  foil  $\rightarrow$  heating in mixture, reddish-brown fumes and soln. acquires a blue color.

Aq. Soln. +  $\text{FeSO}_4$  soln. + con.  $\text{H}_2\text{SO}_4 \rightarrow$  Add reshly  $\text{FeSO}_4$  to nitrate soln. and con.  $\text{H}_2\text{SO}_4$  solwly to soln. downside so that acids fumes a layer beneath the mixture. A brown-ring will form between two liquids.

**(9)  $\text{BO}_3^{-3}$  (Borates)**

Aq. Soln. + con.  $\text{H}_2\text{SO}_4$  and alcohol  $\rightarrow$  if a little borax is mixed with con.  $\text{H}_2\text{SO}_4$  and alcohol in a small porcelain and ignited, green-edge flame

Aq. Soln. +  $\text{AgNO}_3$  soln.  $\rightarrow$  white ppt from concentrate soln. soluble in dil.  $\text{NH}_3$  sol, boiling ppt with  $\text{H}_2\text{O}$  – brown ppt.

Aq. Soln. +  $\text{BaCl}_2$  soln.  $\rightarrow$  white ppt. from concentrate soln. soluble in excess reagent and in  $\text{NH}_3$  salts.

**(10)  $\text{SO}_4^{-2}$  (Sulphates):-**

Aq. Soln. +  $\text{BaCl}_2$  soln.  $\rightarrow$  white ppt insoluble in warm dil.  $\text{HCl}$  and dill.  $\text{HNO}_3$  soluble in boiling con.  $\text{HCl}$ .

Aq. Soln. + lead acetate soln.  $\rightarrow$  white ppt from concentrate soln.

Aq. Soln. + sodium rhodizonate  $\rightarrow$  reddish brown ppt. immediately decolorisation.

Aq. Soln. + mercury nitrate soln.  $\rightarrow$  white ppt of basic.

**(11)  $\text{PO}_4^{-3}$  (Phosphates):-**

Aq. Soln. +  $\text{AgNO}_3$  soln.  $\rightarrow$  yellow ppt soluble in dil.  $\text{NH}_3$  and dil.  $\text{HNO}_3$

Aq. Soln. +  $\text{BaCl}_2$  soln.  $\rightarrow$  white ppt from neutral soln. soluble in dil. Mineral acid and dil.  $\text{CH}_3\text{COOH}$ .

Aq. Soln. + Ammonium molybdate reagent  $\rightarrow$  large excess of reagent yellow ppt.

Aq. Soln. + Mangesia mixture  $\rightarrow$  little aq.  $\text{NH}_3$  excess – white ppt.

Aq. Soln. +  $\text{FeCl}_3$   $\rightarrow$  yellowish white ppt. soluble in dil. Mineral acids.

Aq. Soln. + Cobalt nitrate  $\rightarrow$  heated on a phosphate in charcoal few drops cobalt nitrate-blue mass of phosphate.

Aq. Soln. + Zirconium nitrate reagent  $\rightarrow$  white ppt.

## SPECIAL TESTS FOR ANIONS IN MIXTURE

### (1) Carbonates $\text{CO}_3^{-2}$ in the presence of sulphite $\text{SO}_3^{-2}$

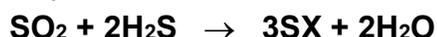
Sulphite interferes in the limewater test of  $\text{CO}_3^{-2}$  as  $\text{CO}_2$  also run limewater milky, hence they can be tested as follows.

Take 1 part of the mixture with it 2 parts  $\text{K}_2\text{Cr}_2\text{O}_7$  in a test-tube and heat it with dil.  $\text{H}_2\text{SO}_4$ . Pass the evolved gas in limewater and observe the changes.

- a) Solution in the test-tube turns green and limewater turns milky.  $\text{CO}_3^{-1}$  and  $\text{SO}_3^{-2}$
- b) Solution in the test-tube turns green and limewater remains unaffected.  $\text{SO}_3^{-2}$
- c) Solution in the test-tube remains unaffected and limewater turns milky  $\text{SO}_3^{-2}$

### (2) Sulphite $\text{SO}_3^{-2}$ , Sulphide $\text{S}^{-2}$ and Sulphate $\text{SO}_4^{-2}$ :-

When the mixture treated with dil.  $\text{H}_2\text{SO}_4$ , it becomes difficult to identify sulphide and sulphite (if both are present together). Only by the small of the gases  $\text{SO}_2$ , and  $\text{H}_2\text{S}$  react together producing sulphur.



Test a portion of  $\text{Na}_2\text{CO}_3$  extract by freshly prepared nitroprusside soln. The appearance a purple color indicates the presence of sulphide. If a positive test is indicated remove the sulphide by adding excess of solid cadmium carbonate or lead carbonate to the sodium carbonate extract, shake it and filter it.

Filterate		Residue
It may contain $\text{SO}_3^{-2}$ and $\text{SO}_4^{-2}$ . Acidify it with dil. HCl and excess of $\text{BaCl}_2$ & filter.		PbS or CdS
Filtrate	Residue	<b><math>\text{S}^{-2}</math> present</b>
It may contain $\text{SO}_3^{-2}$ , Add it $\text{Br}_2$ water or con. $\text{HNO}_3$ , Boil it and add $\text{BaCl}_2 \rightarrow$ white ppt <b><math>\text{SO}_3^{-2}</math> present.</b>	White ppt $\text{SO}_4^{-2}$ present Insoluble in mineral acids.	

### (3) Chloride $\text{Cl}^-$ , Bromide $\text{Br}^-$ and Iodide $\text{I}^-$ :-

Acidify the solution of the mixed halides with dil.  $\text{H}_2\text{SO}_4$  and add solid  $\text{NaNO}_2$  solution, boil. Violet vapors of iodine are liberated which confirm the presence of  **$\text{I}^-$  present.**

Now boil the soln. till no more violet vapors are given off. Add  $\text{NaHCO}_3$  solid till the soln. becomes alkaline and add con.  $\text{HNO}_3$ , boil. brown vapors evolve and soln. becomes brown.  **$\text{Br}^-$  present.**

Boil the soln. till it becomes colorless and add  $\text{AgNO}_3$  soln., a white ppt. soluble in ammonia soln.  **$\text{Cl}^-$  present.**

### (4) Nitrate $\text{NO}_3^-$ And Bromide $\text{Br}^-$ :-

The interfere in the usual test of each other.

**$\text{NO}_3^-$  :-** Take portion of  $\text{Na}_2\text{CO}_3$  extract and acidify it with dill.  $\text{H}_2\text{SO}_4$  Add a piece of Zn boil it.

Now add KI and starch soln. appearance of a blue color indicates.  **$\text{NO}_3^-$  present.**

**$\text{Br}^-$  :-** Take a portion of sodium carbonate extract and acidify it with dil.  $\text{HNO}_3$  and add a few drops of  $\text{CHCl}_3$  or  $\text{CCl}_4$  Now add freshly chloride water with vigorous shaking  **$\text{Br}^-$  present.** If  $\text{CHCl}_3$  or  $\text{CCl}_4$  layer turns orange-yellow color other wise hot.

**(5) Nitrate  $\text{NO}_3^-$  And Iodide  $\text{I}^-$  :-**

Take a portion of sodium carbonate extract, acidify it with dil.  $\text{H}_2\text{SO}_4$ , Add a piece of Zn and boil it. Now add a drop of starch soln. it.

- A deep-blue color indicates the presence of both  $\text{NO}_3^-$  &  $\text{I}^-$ .
- If blue color is obtained, add little KI Soln. Now if a blue color appears then only  $\text{NO}_3^-$  present.

**(6) Nitrate  $\text{NO}_3^-$  And Nitrite  $\text{NO}_2^-$  :-**

If  $\text{NO}_2^-$  is present in the mixture it is not possible test for nitrate, until nitrite is decomposed. First of all nitrite is tested by its usual test. Now in a decomposed test it by brining a KI and starch paper adds the mouth of the test-tube. If its turns blue, it means nitrite is not completely decomposed and hence add more urea or  $\text{NH}_4\text{Cl}$  till the vapors to give blue color with KI and starch paper.

When the nitrite has been composed completely as above add to it dil.  $\text{H}_2\text{SO}_4$  and a piece of Zn. Boil it and then add to KI and starch soln. Blue coloration indicates nitrate.

**(7) Phosphate  $\text{PO}_4^{3-}$  & Arsenate  $\text{AsO}_4^{3-}$  :-**

Both arsenate and phosphate give a yellow ppt. on warming with ammonium molybdate soln. and nitric acid, the later on gently warming and the former on boiling  $\text{PO}_4^{3-}$  &  $\text{AsO}_4^{3-}$ . Acidify the soda extract with dil. HCl, pass in sulphur dioxide it reduce the arsenate to arsenite, boil off the excess  $\text{SO}_2$  (test with  $\text{K}_2\text{Cr}_2\text{O}_7$  paper), and pass  $\text{H}_2\text{S}$  until no more ppt. forms. Filter boil of the  $\text{H}_2\text{S}$ , and test the filtrate for  $\text{PO}_4^{3-}$  by the ammonium molybdate test of with the magnesium nitrate reagent.

**(8) Nitrate  $\text{NO}_3^-$  in the Presence of Bromide  $\text{Br}^-$  and Iodide  $\text{I}^-$  :-**

Treat the substance with NaOH soln. and add Deverba's powder, place in the hot water rack and test for  $\text{NH}_3$  with red litmus paper.

Another produce is to just acidify with soda extract with dill.  $\text{CH}_3\text{COOH}$ , and then add ammonical silver sulphate reagent dropwise until ppt. is complete centrifuge. Add excess con.  $\text{H}_2\text{SO}_4$  cautiously to the centrifugate and apply the brown-ring test.

## Some Useful Reagents, solutions and gases

- Albumin solution** - Dissolve 0.1 g albumin in 20 ml water to obtain a colloidal solution.
- Alizarin** - Shake 2g alizarin,  $C_{14}H_8O_4$ , by adding 10 ml ethanol and use the clear solution for the tests.
- AlizarinredS** - Dissolve 1g alizarin red S (sodium alizarinsulphonate),  $C_{14}H_7O_4 \cdot SO_3Na \cdot H_2O$  in 100ml water.
- Aluminon reagent** - Dissolve 0.1g Aluminon (tri-ammonium arurine-tricarboxylate,  $O:(COONH_4)C_6H_3=C[C_6H_3(OH)OOONH_4]_2$ ) in 100 ml water.
- Ammonium polysulphide** -To 1 liter ammonium sulphide solution(M) add 32 g sulphur, and heat gently until the latter dissolves completely and a yellow solution is formed. The formula of the reagent is  $(NH_4)_2S_x$ , where x is approx. 2.
- Aqua regia** -To 3 volumes of concentrated hydrochloric acid add 1 volume of concentrated nitric acid. Mix and use immediately, the solution does not keep at all.
- Baryta water** -Shake 5 g barium hydroxide octahydrate,  $Ba(OH)_2 \cdot 8H_2O$ , with 100ml water. Allow to stand for 24 hours. Use the clear supernatant liquid for the tests.
- Benzoin  $\alpha$ -oxime (Cupron)** -Dissolve 5g benzoin  $\alpha$ -oxime,  $C_6H_5 \cdot CH(OH) \cdot C(NO) \cdot C_6H_5$ , in 96% ethanol and dilute with the solvent to 100ml.
- 2,2'-Bipyridyl reagent** -Dissolve 0.01 g of the solid reagent in 0.5 ml of 0.1m hydrochloric acid. Alternatively, dissolve 0.01 g reagent in 0.5 ml 96% ethanol.
- Bis-(p-nitrophenyl) carbazide** -Dissolve 0.1 g bis-(p-nitrophenyl) carbazide (p,p'-dinitro-1,5-diphenyl carbazide)  $CO(NH \cdot NH \cdot C_6H_4 NO_2)_2$  in 100ml 96% ethanol.
- Bromine water** -Shake 4g (or 1 ml) liquid bromine with 100 ml water. Ensure that a slight excess of undissolved bromine is left at the bottom of the mixture. The solution keeps for 1 week.
- Bromothymol blue** -Dissolve 40mg bromothymol blue in 100ml 96% ethanol.
- Chloramine-T** -Dissolve 14.1 g chloramine-T,  $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot N \cdot NaCl \cdot 3H_2O$ , in water and dilute to 1 liter.
- Chlorine gas** -This gas is available commercially in steel cylinders and should be taken from these. Alternatively it can be produced in a Kipp apparatus (with glass joints only) from calcium hypochlorite (bleaching powder) and 6M hydrochloric acid. It is advisable to mix the bleaching powder with some gypsum powder, making the mixture wet, to produce lumps of the reagent. After drying, these lumps can be placed into the Kipp apparatus.
- Chlorine water** -Saturate 200ml of water with chlorine gas.
- Chromic acid** -Pour 25 ml chromosulphuric acid cautiously, with constant stirring, into 70ml water. After cooling, dilute the solution with water to 100ml.
- Cupferron** -Dissolve 2g cupferron,  $C_6H_5 \cdot N(NO)ONH_4$ , in 100ml water. The solution does not keep well. Addition of 1 g ammonium carbonate,  $(NH_4)CO_3$ , enhances the stability.
- Diazine green** -Dissolve 0.01 g diazine green in 100 ml water.
- Dimethyl glyoxime** -Dissolve 1 g dimethyl glyoxime,  $CH_3 \cdot C(NO) \cdot C(NO) \cdot CH_3$ , in 100ml 96% ethanol.
- Diphenylthiocarbazon (dithizone)** -Dissolve 5 mg diphenylthiocarbazon (dithizone),  $C_6H_5 \cdot N:N \cdot CS \cdot NH \cdot NH \cdot C_6H_5$ , in 100 ml chloroform.

**Dithio-oxamide (rubeanic acid)**

-Dissolve 0.5g dithio-oxamide  $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{CS}\cdot\text{NH}_2$  in 100ml of 96% ethanol. The solution decomposes rapidly and should be prepared freshly each time.

**Ferron**

-Dissolve 0.2g ferron (8-hydroxy-7-iodoquinoline-5-sulphonic acid),  $\text{C}_9\text{H}_6\text{O}_4\text{NSI}$ , in 100ml water.

**Fluorescein reagent**

-To 1 g fluorescein,  $\text{C}_{20}\text{H}_{12}\text{O}_5$ , add a mixture of 50 ml 96% ethanol and 50 ml water. Shake, allow to stand for 24 hours, and filter the solution.

**Fuchsin**

-Dissolve 0.1 g fuchsin in 100ml water.

**Hydrogen sulphide gas**

-The gas can be obtained from a Kipp apparatus, using solid Iron(II) sulphide,  $\text{FeS}$ , and 6M hydrochloric acid. The gas can be washed by bubbling it through water.

**8-Hydroxyquinoline ( $\text{C}_9\text{H}_7\text{ON}$ )**

-5 g 8-hydroxyquinoline, in a mixture of 90 ml water and 10 ml of sulphuric acid.

**Indigo solution**

-Dissolve 0.1 g indigo ( $\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2$ ) in 10 ml concentrated sulphuric acid.

**Indole**

-Dissolves 15mg indol ( $\text{C}_8\text{H}_7\text{NH}\cdot\text{CH}\cdot\text{CH}$ ) in 100 ml 96% ethanol.

**Lime water**

-Dissolve 5 g calcium hydroxide,  $\text{Ca}(\text{OH})_2$  in 100 ml water. Allow to stand for 24 hours and use the clear supernatant liquid for the tests.

**Magnesia mixture**

-Dissolve 102g magnesium chloride hexahydrate,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , and 107 g ammonium chloride,  $\text{NH}_4\text{Cl}$ , in water, dilute to 500ml, add 50ml concentrated ammonia and dilute the solution to 1 litre with water.

**Manganese(II) nitrate-silver nitrate reagent**

-Dissolve 2.87g manganese(II) nitrate hexahydrate,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , in 40ml water. Add a solution of 3.55g silver nitrate,  $\text{AgNO}_3$ , in 40 ml water and dilute the mixture to 100 ml. Neutralize the solution with 2M sodium hydroxide until a black precipitate is starting to form. Filter and keep the solution in a dark bottle.

**Manganese(II) nitrate-silver nitrate-potassium fluoride reagent**

-To 100ml manganese(II) nitrate-silver nitrate reagent add a solution of 3.5 g potassium fluoride in 50 ml water. Boil, filter off the dark precipitate in cold, and use the clear solution for the tests.

**Mercury(I) chloride (calomel) suspension**

- To 5ml of 0.05M mercury(I) nitrate add 1 ml of 2M hydrochloric acid. Wash the precipitate 5 times with 10ml water by decantation. Suspend the precipitate finally with 5 ml water.

**Methylene blue**

- Dissolve 0.1 g methylene blue in 100 ml water.

**1-Naphthylamine**

- Boil 0.3g 1-naphthylamine  $\text{C}_{10}\text{H}_7\text{NH}_2$  with 70ml water for a few minutes. Filter or decant the clear liquid To the cold solution add 30ml glacial acetic acid.

**Nessler's reagent**

- Dissolve 10g potassium iodide in 10 ml water (solution a) Dissolve 6 g mercury(II) chloride in 100 ml water (solution b). Dissolve 45g potassium hydroxide in water and dilute to 80ml (solution c). Add solution b to solution a dropwise until a slight permanent precipitate is formed, then add solution c, mix, and dilute with water to 200ml. Allow to stand overnight and decant the clear solution, which should be used for the test.

**Nickel ethylenediamine nitrate reagent**

-This reagent should be prepared when required from 2ml 0.5M nickel chloride solution by adding ethylenediamine dropwise, until a violet colour appears. The colour is due to the formation of the complex ion  $[\text{Ni}(\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 - \text{NH}_2)_3]^{2+}$

**Nitrazine yellow**

- Dissolve 0.1 g of nitrazine yellow (2,4-dinitrobenzeneazo) 1-naphthol-4,8-disulphonic acid, disodium salt in 100ml water.

**Nitric acid**

- The commercial concentrated nitric acid is a water-like solution with a density of  $1.42\text{gcm}^{-3}$ . It contains 69.5% (w/w)  $\text{HNO}_3$  or  $0.99\text{g HNO}_3 \text{ ml}^{-1}$ . It is approx. 15.6 molar. Nitrous fumes make the partially decomposed reagent reddish-brown. It should be handled with utmost care, wearing gloves and eye protection.

**2- Nitrobenzaldehyde-** Dissolve 5mg of 2-nitrobenzaldehyde,  $\text{NO}_2 \text{ C}_6\text{H}_4 \text{ CHO}$ , in 1ml of 2M sodium hydroxide.

**Nitron reagent**

- Dissolve 5g nitron ( $\text{C}_{20}\text{H}_{16}\text{N}_4$ ) in 100 ml 2M acetic acid.

**Oxalic acid**

- Shake 1g oxalic acid dihydrate,  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ , with 10 ml water, and use the clear supernatant liquid for the tests.

**Perchloric acid**

- The concentrated perchloric acid solution is a clear, colourless liquid with a density of  $1.54\text{gcm}^{-3}$  and contains 60% (w/w)  $\text{HClO}_4$  (or  $0.92 \text{ g HClO}_4$  per ml). It is approximately 9.2 molar.

**1,10-Phenanthroline-** Dissolve 0.1 g 1,10-phenanthroline hydrate,  $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$ , in 100ml water.

**Phenolphthalein**

- Dissolve 0.5g phenolphthalein.  $\text{C}_6\text{H}_4(\text{COOH}) \text{ CH}(\text{C}_6\text{H}_4\text{OH})_2$ , in 100ml 96% ethanol.

**Phenylhydrazine reagent**

- Dissolve 1g phenylhydrazine,  $\text{C}_6\text{H}_5 \text{ NH NH}_2$ , in 2 ml glacial acetic acid.

**Phosphomolybdic acid** - Dissolve 0.5g dodecamolybdophosphoric acid icositetrahydrate,  $\text{H}_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 24\text{H}_2\text{O}$ , in 10ml water. The solution does not keep well.

**Phosphoric acid**

- Concentrated phosphoric acid is a viscous, clear, colourless liquid with a high density ( $1.75\text{gcm}^{-3}$ ). It contains 88 per cent (w/w)  $\text{H}_3\text{PO}_4$  (or  $1.54\text{g H}_3\text{PO}_4$  per ml) and is approximately 16 molar.

**Picrolonic acid (picrotic acid)**

- Shake 1g picrolonic acid,  $\text{C}_{10}\text{H}_8\text{O}_5\text{N}_4$ , with 5ml water and use the clear supernatant liquid for the tests.

**Potassium cyanide** - Dissolve 1g potassium cyanide, KCN. 10 ml water. Discard the solution immediately after use. **(POISON)**

**Pyridine**

- The pure solvent is a clear, colourless liquid with a characteristic odour. It has a density of  $0.98 \text{ g cm}^{-3}$  and boils at  $113^\circ\text{C}$ .

**Pyrogallol (10%)**

- Dissolve 0.5g pyrogallol,  $\text{C}_6\text{H}_3(\text{OH})_3$  in 5ml water. The reagent decomposes slowly.

**Pyrrole**

- Dissolve 1 g pyrrole,  $\text{C}_4\text{H}_5\text{N}$ , in 100ml of (aldehyde-free) 96% ethanol.

**Quinalizarin (in NaOH)**

- Dissolve 0.05g quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) in a mixture of 50 ml water and 5 ml 2M sodium hydroxide. Dilute the solution with water to 100 ml.

**Quinalizarin (in pyridine)**

- Dissolve 0.01g quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) in 2ml pyridine, and dilute the solution with acetone to 20ml.

- Rhodamine-B** - Dissolve 0.01 g rhodamine-B,  $C_{28}H_{31}N_2O_3$  in 100ml water. A more concentrated reagent can be prepared by dissolving 0.05g of Rhodamine-B in 100 ml solution containing 15g of potassium chloride in 2M hydrochloric acid.
- Rochelle salt** - Potassium sodium tartrate.
- Salicylaldehyde oxime (salicylaldoxime)**  
- Dissolve 1g salicylaldoxime  $C_6H_4 - CH(NO_2) \cdot OH$ , in 5 ml cold 96% ethanol and pour the solution dropwise into 95ml water at a temperature not exceeding  $80^\circ C$ . Shake the mixture until clear, and filter if necessary.
- Sodium azide-iodine reagent**  
- Dissolve 3 g sodium azide,  $NaN_3$ , in 100ml 0.05M iodine (sodium tri-iodide) solution.
- Sodium carbonate-phenolphthalein reagent**  
- Mix 1 ml 0.005M sodium carbonate with 2 ml 0.5% phenolphthalein and dilute with water to 10 ml.
- Sodium dithionite** - Dissolve 10.5 g sodium dithionite dihydrate,  $Na_2S_2O_4 \cdot 2H_2O$ , in water and dilute to 100 ml. The solution should be freshly prepared.
- Sodium nitroprusside reagent**  
- Rub 0.5g sodium nitroprusside dihydrate,  $Na_2[Fe(CN)_5NO] \cdot 2H_2O$  in 5 ml water. Use the freshly prepared solution.
- Sodium peroxide** - Dissolve 3.9g sodium peroxide,  $Na_2O_2$ , in water and dilute to 100ml. The solution must be prepared freshly.
- Sodium rhodizonate**-Dissolve 0.5g sodium rhodizonate (rhodizonic acid sodium salt,  $C_6O_6Na_2$ ) in 100 ml water. The solution decomposes rapidly.
- Starch solution** - Suspend 0.5g soluble starch in 5 ml water, and pour this into 20ml water, which has just ceased to boil. Mix. Allow to cool, when the solution becomes clear.
- Sulphanilic acid reagent**  
- (1 %). Dissolve 1 g sulphanilic acid (4-aminobenzenesulphonic acid,  $H_2N-C_6H_4-SO_3H$ ) in 100ml 30% warm acetic acid and allow to cool.
- Sulphur dioxide gas** - This gas is available commercially in a liquefied state in aluminium canisters, from which it can be taken. Alternatively it can be produced from sodium sulphite and 8M sulphuric acid. The solid reagent should be placed into a round-bottomed flask, which can be heated. The acid is kept in a funnel with a stopcock, inserted into one opening of the flask. By adding some sulphuric acid to the solid and by gentle heating, sulphur dioxide gas comes through the second opening of the flask and can be washed in concentrated sulphuric acid.
- Sulphuric acid** - The commercial reagent is a colourless, oil-like liquid of a high density ( $1.84 \text{ g cm}^{-3}$ ). It contains 98% (w/w)  $H_2SO_4$  (or 1.76g  $H_2SO_4$  per ml) and is approximately 18 molar. The reagent must be handled with utmost care, wearing rubber gloves and eye protection. When diluting, concentrated sulphuric acid must be poured slowly into water, while stirring and, if necessary, cooling. Traces of the reagent have to be removed immediately from the skin or from clothing by washing with large amounts of water.
- Tannic acid** - Dissolve 5g tannic acid.  $C_{76}H_{52}O_{46}$  in 100ml water and filter the solution.
- Titan yellow** - Dissolve 0.1 g Titan yellow in 100 ml water.

**Triethanolamine** -  $N(CH_2CH_2-OH)_3$ . The commercial liquid is a viscous liquid with a density of  $1.12g\text{ cm}^{-3}$

**Uranyl magnesium acetate reagent**

- Dissolve 10g uranyl acetate dihydrate,  $UO_2(CH_3COO)_2 \cdot 2H_2O$ , in a mixture of 6ml glacial acetic acid and 100ml water (solution a). Dissolve 33g magnesium acetate tetrahydrate,  $Mg(CH_3COO)_2 \cdot 4H_2O$ , in a mixture of 100 ml glacial acetic acid and 100 ml water (solution b). Mix the two solutions, allow to stand for 24 hours, and filter.

**Uranyl zinc acetate reagent**

- Dissolve 10g uranyl acetate dihydrate,  $UO_2(CH_3COO)_2 \cdot 2H_2O$ , in a mixture of 5ml glacial acetic acid and 20ml water, and dilute the solution to 50 ml (solution a). Dissolve 30g zinc acetate dihydrate,  $Zn(CH_3COO)_2 \cdot 2H_2O$ , in a mixture of 5 ml glacial acetic acid and 20 ml water, and dilute with water to 50ml (solution b). Mix the solutions, add 0.5g sodium chloride, NaCl, allow to stand for 24 hours and filter.

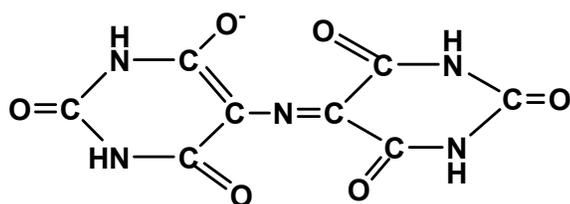
**Zirconium nitrate reagent**

- Heat 10g commercial zirconium nitrate,  $ZrO(NO_3)_2 \cdot 2H_2O$ , and 100ml 2m nitric acid to boiling, stirring constantly. Allow to cool and set aside for 24 hours. Decant the clear liquid and use this for the tests.

## INDICATORS & REAGENTS

**Murexide (Ammonium Purpurate)-**

It is an Ammonium salt of purpuric acid.

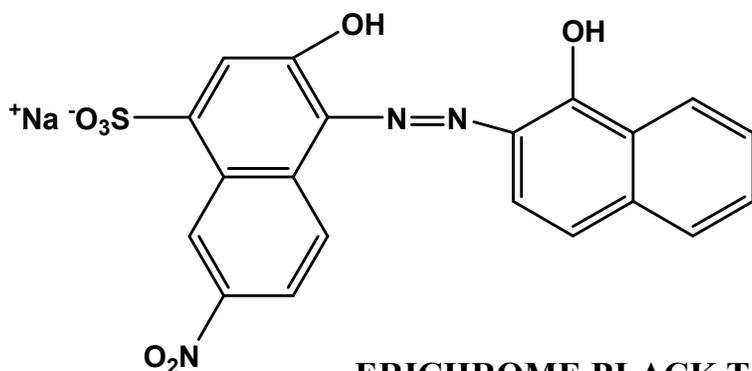


**MUREXIDE**

Used for the analysis of Cu(orange), Ni(yellow), Co(yellow) and Ca(red) by EDTA titration in basic medium. Dissolve 0.5g of murexide in water and after shaking thoroughly use supernatant liquid, or mix murexide with pure NaCl or  $NH_4Cl$  in the ratio of 1:500 and use 0.1-0.5g for the titration.

**Eriochrome Black T (Solochrom Black) -**

Sodium salt of 1-(1-hydroxy-2-naphthylazo) -6-nitro-2-naphthol-4-sulphonate(II).

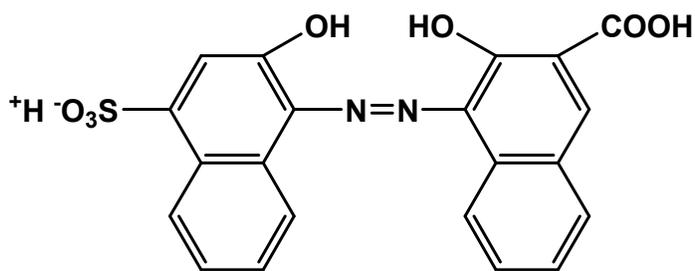


**ERICHRROME BLACK T**

Used for the analysis of Zn, Cd, Mg, Mn, Cu, Ni, Co and Al by EDTA titration in acidic medium. Dissolve 0.2g of EBT in 15ml triethanolamine and 5ml ethanol for the titration.

**Patton and reeders's indicator**

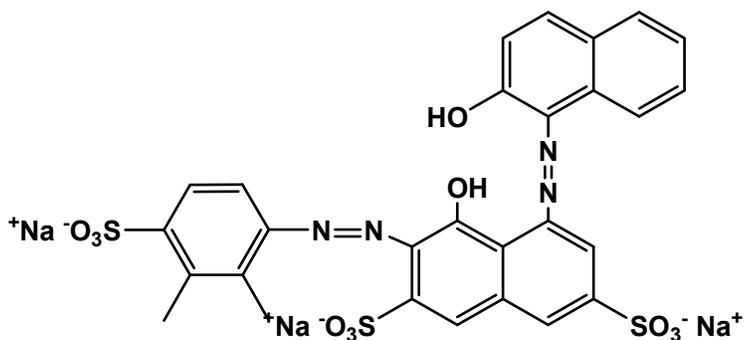
[2-hydroxy-1(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid(III)]



Used for the direct titration of Ca in presence of Mg by EDTA titration in basic medium. Mix 0.5g of Patton and reeders's indicator with 10g Na<sub>2</sub>SO<sub>4</sub> and use 1g for the titration.

**Patton & reeder's indicator****Fast Sulphon Black F-**

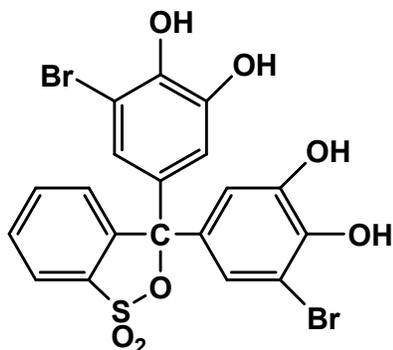
Sodium salt of 1-hydroxy-8-(2-hydroxynaphthylazo)-2-(sulphonaphthylazo)-3,6-disulphonic acid(III)

**FAST SULPHONE BLACK-F**

Used for the direct titration of Cu and Ni by EDTA in basic medium. Mix 5g of Fast sulphon Black F in 100ml water for the titration.

**Bromopyrogallol Red –**

Dibromopyrogallol sulphonphthalein(IX)

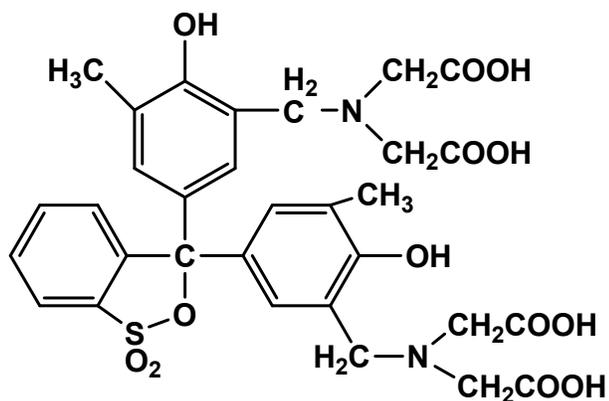


It has acid-base properties. Mix .05g of Bromopyrogallol Red in 100ml of 50% ethanol for the titration.

**BROMOPYROGALLOL RED**

**Xylenol Orange –**

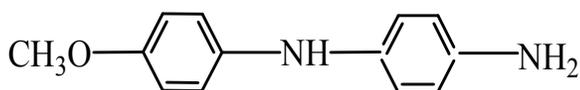
3,3'-bis[N,N'-di(Carboxymethyl)-aminomethyl]-o-cresol sulphonaphthalein(X)

**XYLENOL ORANGE**

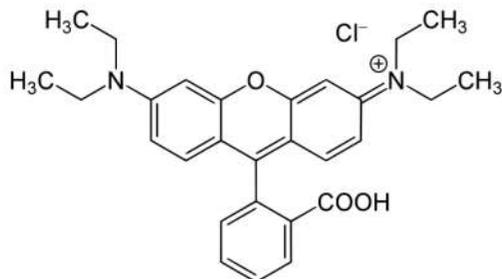
Used for the direct titration of Zn,Cd,Pb, Co,Bi,Th,etc. by EDTA in basic medium. Mix 0.5g of Xylenol Orange in 100ml water for the titration.

**Variamine Blue**

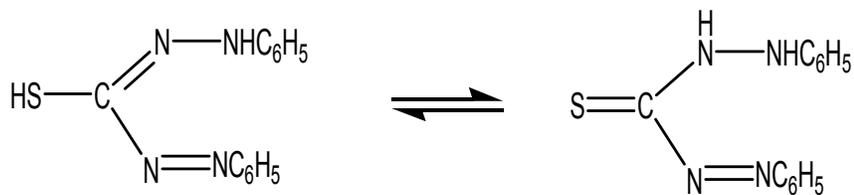
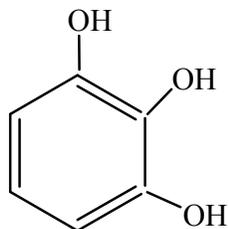
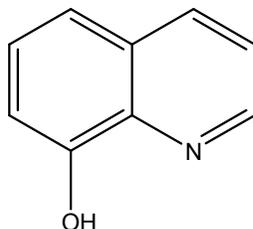
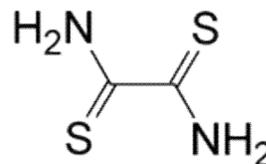
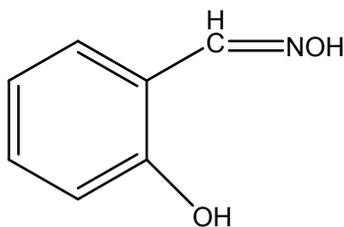
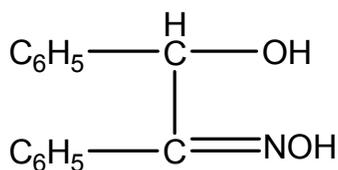
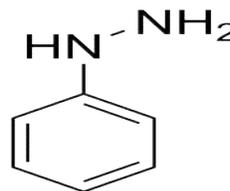
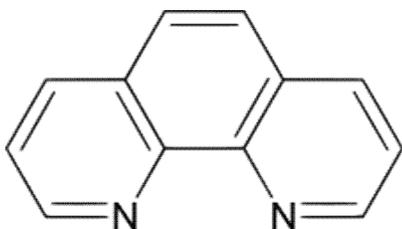
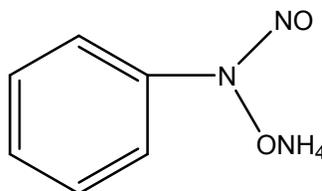
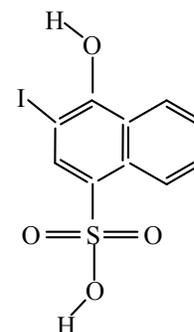
4-methoxy-4'-amino-diphenylamine

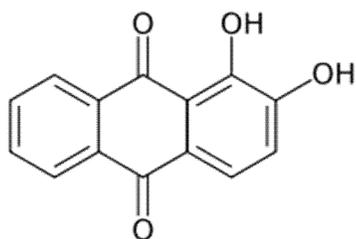
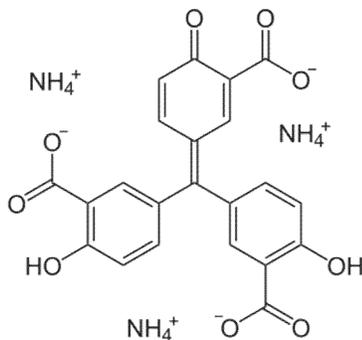
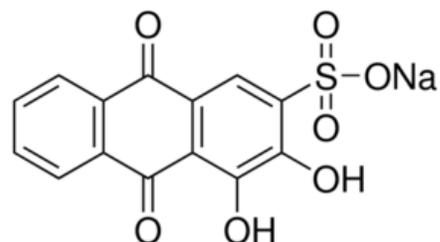
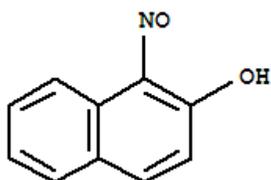
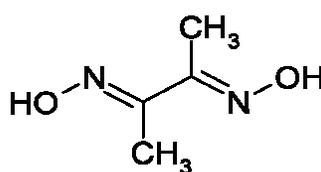
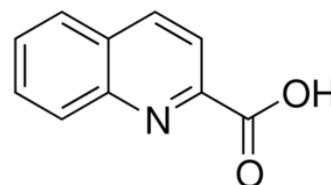
**Variamine Blue**

Used for the complexometric titration of Fe(III) by EDTA. Mix 1g of Variamine blue in 100ml water for the titration.

**Rhodamine-B (Sb)-****Rhodamine-B**

Soluble in water (50 g/L), and soluble in acetic acid solution (30 vol.%) 400 g/L. Chlorinated tap water decomposes rhodamine B. Its solutions adsorb to plastics so should be kept in glass.

**Dithiozone (For Pb,Zn)****DITHIZONE****Pyrogallol (For Bi)****8-Hydroxyquinoline (For Bi)****Rubeanicacid (For Cu)  
(Dithiooxamid)****Salicylaldoxime (For Cu)****Cupron (For Cu,Mo)  
Benzoin- $\alpha$ -oxime****Phenylhydrazine(For Mo)****1,10 phenanthroline(For Fe(II))****Cupferron (For Fe(III),Ti)****Ferron (For Fe(III))**

**Alizarin (For Al)****Aluminon (For Al)****Alizarin red S (For Zr)****1-nitroso-2-naphthol (For Co,Ni)****DMG (For Ni)****Quinaldic Acid (For Zn)****Some Other useful reagents**

2,2' Bipyridyl (For Fe(II))

Na-rhodizonate(Ba,Sr)

Oxine(Mg)

Diazine (Sn)

Diphenyl carbazide(Mg)

Titan Yellow(Mg)

Na-diyodxytartrate(Ca)

Quinalizarin(Mg)

Indole(NO<sub>2</sub><sup>-</sup>)