SYSTEMATIC ANALYSIS OF INORGANIC SALT MIXTURE

II B.Sc. CHEMISRY PRACTICALS

PG DEPARTMENT OF CHEMISTRY

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SYSTEMATIC INORGANIC QUALITATIVE ANALYSIS

The given unknown inorganic mixture contains two inorganic salts. Each salt contains anion and a cation. One of the two anions, is an interfering anion and the other one is a non-interfering anion.

The list of non-interfering anion is given below

1. Carbonate anion 2. Sulphide anion 3. Sulphate anion 4. Nitrate anion 5. Chloride anion 6. Bromide anion

The list of interfering anions, is given below

1. Fluoride anion 2. Borate anion 3. oxalate anion 4. Phosphate anion

The group wise list of cations, is given below :

Group I	Group II	Group III	Group IV	Group V	Group VI
1. Lead	1. Copper	1. Iron	1. Cobalt	1. Barium	1. Ammonium
	2. Bismuth	2. Aluminium	2. Nickel	2. Strontium	2. Magnesium
	3. Cadmium		3. Manganese	3. Calcium	
			4. Zinc		

Analysis of anions must be done first followed by the analysis of cations
It is necessary to do all the available tests for the anions
It is essential to record all the alterations as and when they are made
Negative reactions should not be ignored and should be recorded

PRELIMINARY TESTS

1. Visual Examination of the Sample

NO	EXPERIMENT	OBSERVATION	INFERENCE
I)	COLOUR The colour of the given mixture is examined	a) Black b) Blue c) Brown d) Green e) Pink f) No characteristic colour	May be Pb, Cu, Fe or Ni salt May be Cu or Fe salt May be Pb, Fe or Bi salt May be Fe, Cu or Ni salt May be Co salt May not be Pb, Bi, Cu, Fe, C, Ni etc.

I) i)	ACTION OF HEAT A small amount of the given mixutre, is taken in a dry test tube and heated strongly	a) Becomes black b) Yellow when hot and white when cold c) Colourless and odourless gas, turning lime water milky $CO_{3}^{2-} \rightarrow O^{2-} + CO_2$ $CO_2 + Ca(OH)_2 \rightarrow H_2O + CaCO_3$(milky) d) Colourless gas with the smell of burnt sulphur, turning potassium dichromate paper, green $2S^{2-} + 3O_2 \rightarrow 2O^{2-} + 2SO_2$ (smell of burnt S] $3SO_2 + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3SO_3 + 4H_2O + 2\,Cr^{3+}$ (green) e) Colourless gas with the smell of burnt sulphur, turning potassium dichromate paper, green $SO_3^{2-} \rightarrow O^{2-} + SO_2$ (smell of burnt sulphur) $3SO_2 + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3SO_3 + 4H_2O + 2\,Cr^{3+}$ (green) f) Colorless gas with the smell of ammonia $NH_4^+ \rightarrow H^- + NH_3$ (smell of ammonia) g) Colourless gas, burning with a blue flame $(COO)_2^{2-} \rightarrow O^{2-} + CO + CO_2$(blue flame) h) Reddish-brown gas, turning ferrous sulphate paper, brown $4\,NO_3^- \rightarrow 2O^{2-} + O_2 + 4\,NO_2$ (reddish-brown) (I) No characteristic reaction	May be copper salt May be zinc salt May be carbonate or oxalate anion May be sulphide anion May be sulphate anion May be ammonium salt May be oxalate anion My be nitrate anion May not be carbonate, sulphide, sulphite, oxalate nitrate etc.

ii)	FLAME COLOURATION a) a small amount of the given mixture is mixed with a drop of conc. HCl to make a paste. This paste is introduced at the base of the outer oxidizing region of the non-luminous flame of the bunsen burner	a) Brick – red flame b) Crimson-red flame c) Green flame d) No characteristic colouration	May be calcium salt May be strontium salt May be Ba, Cu or borate salt Absence of Ba, Ca and Sr salt
iii)	A small amount of the given mixture is mixed with an equal amount of calcium fluoride salt and a drop of Conc H_2SO_4 to make a paste. This paste is introudced at the base of the outer oxidizing region of the non-luminous flame of the bunsen burner.	Green-edged flame appears $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ HF$ $B_2O_3 + 3\ HF \rightarrow 3\ H_2O + 2BF_3$ (green flame)	Presence of borate anion
iv)	A small amount of the given mixture is mixed with an equal amount of borax salt and a drop of conc. H_2SO_4 to make a paste. This paste is introduced at the base of the outer oxidizing region of the non-luminous flame of the bunsen burner.	Green edged flame appears No green-edged flame appears	Presence of fluoride anion Absence of fluoride anion
v)	Ethyl borate test A small amount of the given mixture is taken in a test tube and heated with a few drops of ethanol and conc H_2SO_4. the gas evolved, is introduced at the base of the outer oxidizing region of the non-luminous flame of the bunsen burner.	Green edged flame appears $BO_3^{3+} + 3H^+ \rightarrow H_3BO_3$ $H_3BO_3 + 3\ EtOH \rightarrow (Et)_3BO_3 + 3\ H_2O$ No green-edged flame	Presence of borate anion Absence of borate anion
2. i)	PRELIMINARY EXAMIANTION FOR ANIONS ACTION OF DILUTE HCl A small amount of the given mixture is taken in a test tube and treated / heated with a few drops of dilute HCl	(a) Brisk effervescence of a colourless, odourless gas, turning lime water, milky. $CO_{3}^{2-} + 2H_{+} \rightarrow H_2O + CO_2$ (Colourless gas) $CO_2 + Ca(OH)_2 \rightarrow H_2O + Ca\ CO_3$ (milky) b) Colourless gas with rotten-egg smell, turning lead acetate paper,	May be carbonate anion May be sulphide anion

		black and alkaline nitroprusside paper red. $S^{2-} + 2H^{+} \rightarrow H_2S$ $H_2S + Pb(OAc)_2 \rightarrow HOAc + Pb S$ (black)	
		c) Colourless gas with the smell of burnt sulphur, turning acidified potassium dichromate paper, green $SO_3^{2-} + 2H \rightarrow H_2O + SO_2$ (smell of burnt S) $3 SO_2 + CrO_7^{2-} + 8 H^{+} \rightarrow 3 SO_3 + 4H_2O + 2Cr_3^{+}$ (green) d)Redish brown gas evolves and the solution becomes blue in colour $NO^{2-} + H^{+} \rightarrow HNO_2$ $3HNO_2 \rightarrow H_2O + HNO_3 + 2NO$ $2NO + O_2 \rightarrow 2NO_2$(reddish-brown gas) $NO_3^{-} + H^{+} \rightarrow HNO_3$ $4HNO_3 \rightarrow H_2O + O_2 + 4NO_2$(reddish-brown gas) d) No characteristic reaction	May not be carbonate, sulphide and sulphite anion
ii)	ACTION OF CON. HCl	a)Brisk effervescence of a colourless, odourless gas, turning lime water, milky. $CO_{3_{2-}} + 2H_{+} \rightarrow H_2O + CO_2$ (Colourless gas) $CO_2 + Ca(OH)_2 \rightarrow H_2O + Ca CO_3$ (milky) b) Colourless gas with rotten-egg smell, turning lead acetate paper, black and alkaline nitroprusside paper red. $S^{2-} + 2H^{+} \rightarrow H_2S$ $H_2S + Pb(OAc)_2 \rightarrow HOAc + Pb S$ (black)	May be carbonate anion May be sulphide anion

		c) Colourless gas with the smell of burnt sulphur, turning acidified potassium dichromate paper, green $SO_3^{2-} + 2H \rightarrow H_2O + SO_2$ (smell of burnt S) $3\ SO_2 + CrO_7^{2-} + 8\ H^+ \rightarrow 3\ SO_3 + 4H_2O + 2Cr_3^+$ (green) d) No characteristics reaction	May not be carbonate, sulphide and sulphite anion
iii)	ACTION OF DILUTE H_2SO_4 AND $KMnO_2$ A small amount of the given mixture is taken in a test tube and treated with a few drops of dilute H_2SO_4 and $KMnO_4$ solution.	(a) Pink colour disappears immediately in cold condition $2.\ MnO_4 + 5\ NO_2^- + 8H^+ \rightarrow 5\ NO_3^- + 3H_2O + 2\ Mn^{2+}$ (b) Pink colour disappears only slowly. (c) Pink colour disappears only on heating $2\ MnO_4^- + 16\ H^+ + 5\ (COO)_2^{2-} \rightarrow 10\ CO_2 + 8\ H_2O + 2\ Mn^{2+}$ d) No characteristics reaction	May not be carbonate, sulphide and sulphite anion
iv)	ACTION OF DILUTE H_2SO_4 AND MnO_4 A small amount of the given mixture is mixed with an equal amount of MnO_2 powder and heated with dilute H_2SO_4 in a test tube.	(a) Brisk effervescence of a colourless, odourless gas, turning lime water, milky $CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$ (colourless gas) $CO_2 + Ca(OH)_2 \rightarrow H_2O + CaCO_3$ (milky) b) Brisk effervescence of a colourles, odourless gas, turning lime water, milky $MnO_2 + 4H^+ + (COO)_2^{2-} \rightarrow Mn^{2+} + 2H_2O + 2CO_2$ $CO_2 + Ca(OH)_2 \rightarrow H_2O + CaCO_3$ (milky) (c) No characteristic reaction	Presence of carbonate anion May be oxalate anion (colourless gas) May not be carbonate or oxalate anion
V	ACTION OF CONC H_2SO_4 AND MnO_2 A small amount of the given mixture is mixed with an equal amount of MnO_2 powder and heated with conc. H_2SO_4 in a test tube	(a) Greenish-yellow gas with pungent smell. turning starch potassium iodide paper, blue	May be chloride anion May be bromide anion

		$MnO_2 + 4H^+ + 2Cl^- \rightarrow Mn^{2+} + 2H_2O + Cl_2$ (greenish – Yellow gas) b) Reddish-brown gas condensing to a red liquid $MnO_2 + 4H^+ + 2Br \rightarrow Mn^{2+} + H_2O + Br_2$ (reddish-brown gas) c) No characteristic reaction	May not be chloride and bromide anion
VI	ACTION OF CONC H_2SO_4 A small amount of the given mixture is taken in a test tube and heated strongly with a few drops of conc. H_2SO_4	(a) Colourless gas with a glass rod dipped in ammonium hydroxide solution $Cl^- + H^+ \rightarrow HCl$ $HCl + NH_4OH \rightarrow H_2O + NH_4Cl$ (fumes O_2 the glass rod) b) Brisk effervescence of a colourless, odoourless gas, turning lime water, milky $CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$ (Colourless gas) $CO_2 + Ca(OH)_2 \rightarrow H_2O + CaCO_3$ (milky) c) Brisk effertvescence of a colourless, odourless gas, turn lime water, milky. $(COO)_2^{2-} + 2H^+ \rightarrow H_2O + CO + CO_2$ $CO_2 + Ca(OH)_2 \rightarrow H_2O + Ca CO_3$ (milky) d)Colourless gas giving white precipitate with a glass rod dipped in water, and oily appearance at the inner walls of the test tube. $F^- + H^+ \rightarrow HF$ SiO_2 (glass) + 4 HF $\rightarrow 2H_2O + SiF_4$ + (White precipitate) $SiF_4 + 4 H_2O \rightarrow 4 HF + Si(OH)_4$ (oily appearance) e) Reddish-brown gas, turning fluorescence paper, red.	May be chloride anion May be carbonate anion May be oxalate anion Presence of fluoride anion Maybe bromide anion

		$Br^- + H_2SO_4 \rightarrow 2\ H_2O + SO_2 + Br_2$ (reddish-brown gas) f) Reddish-brown gas, turning Ferrous sulphate paper, brown $NO_{2\_} + H_+ \rightarrow HNO_2$ $HNO_2 \rightarrow HNO_3 + H_2O + 2NO$ (reddish – brown gas) $HNO_2 + HNO_3 \rightarrow H_2O + 2NO$(reddish-brown gas) $FeSO_4 + NO + 5\ H_2O \rightarrow [Fe(H_2O)_5NO]\ SO_4$ brown $NO_3^- + H^+ \rightarrow HNO_3$ $4HNO_3 \rightarrow 2H_2O + O_2 + 4NO_2$ (reddish-brown gas) h)No characteristic reaction	May be nitrite anion May be nitrate anion Absence of carbonate, oxalate, fluoride, bromide nitrite, nitrate etc.,
vii)	ACTION OF CONC. H_2SO_4 AND COPPER TURNINGS A small amount of the given mixture is taken in a test tube and heated strongly with a few pieces of copper turnings and conc. H_2SO_4	(a) reddish – brown gas, turning ferrous sulphate paper, brown $NO_{3\_} + H_+ \rightarrow HNO_3$ $4HNO_3 \rightarrow H_2O + O_2 + 4NO_2$ (reddish – brown gas) b) Reddish-brown gas, turns fluorescence paper, red. $Br^- + H_2SO_4 \rightarrow 2\ H_2O + SO_2 + Br_2$ (reddish-brown gas) c) No characteristic reaction.	May be nitrate anion May be bromide anion May not be nitrate or bromide anion
viii)	ACTION OF $AgNO_3$ SOLUTION		

	A small amount of the given mixture is dissolved in dilute H_2SO_4 in a test tube and a few drops of dilute $AgNO_3$ solution are added.	a) A white precipitate, soluble in dilute HNO_3 forms a black precipitate on boiling $SO_3^{2-} + 2\ Ag^+ \rightarrow Ag_2\ SO_3$ (white precipitate) 2. $Ag_2\ SO_3 \rightarrow O_2 + 2\ SO_2 + 4$ Ag (black precipitate) b) A black precipitate, insoluble in cold dilute HNO_3 but dissolves on heating. $S^{2-} + AgNO_3 \rightarrow NO_3^- + Ag_2S$ (black precipitate) (c) No characteristic reaction	May be sulphite anion May be sulphide anion May not be sulphide or sulphite anion
ix)	ACTION OF $BaCl_2$ SOLUTION A small amount of the given mixture is dissolved in dilute HCl in a test tube and a few drops of dilute $Bacl_2$ solution are added	a) A white precipitate soluble in dilute HCl $SO_3^{2-} + BaCl_2 \rightarrow 2\ Cl^- + Ba\ SO_3$ (white precipitate) b) A white precipitate, insoluble in hot dilute HCl and dilute HNO_3 $SO_4^{2-} + BaCl_2 \rightarrow 2\ Cl^- + BaSO_4$(white precipitate) (c) No characteristic reaction	May be sulphite anion May be sulphate anion May not be sulphite or sulphate anion
x)	CHROMYL CHLORIDE TEST A small amount of the given mixture is taken in a test tube and heated strongly with a title of Potassium dichromate and conc. H_2SO_4	a) Orange-red vapours. condensing to a red liquid forms yellow precipitate with Pb $(OAc)_2$ $Cl^- + H^+ \rightarrow HCl$ $Cr_2O_{7_{2-}} + 2H_+ \rightarrow H_2O + 2\ CrO_3$ $CrO_3 + 2HCl \rightarrow H_2O + CrO_2Cl_2$ $CrO_2Cl_2 + 2H_2O \rightarrow 2\ HCl + H_2CrO_4$ $H_2CrO_4 + Pb\ (OAc)_2 \rightarrow 2\ HOAc +$ Pb CrO_4 (Yellow precipitate)	Presence of chloride anion Absence of chloride anion

		(b) No characteristic reaction	
xi)	ACTION OF CONC HNO_3 A small amount of the given mixture is taken in a test tube and warmed with a few drops of conc. HNO_3 till no more brown fumes evolve and then 2 cc of ammonium molybdate reagent is added to it.	a) Canery yellow precipitate appears in cold on shaking or on slight heating on vigorous boiling b) No characteristic reaction	Presence of phosphate anion Absence of phosphate or arsenate anions
xii)	ACTION OF NEUTRAL $FeCl_3$ A small amount of the given mixture is taken in a test tube and warmed with a few drops of dilute HCl and a few drops of Fe Cl_3 are added	a) A pale – yellow precipitate appears $PO_4^{3-} + FeCl_3 \rightarrow 3\ Cl^- + FePO_4$ (pale-yellow precipitate) b) No characteristic reaction	Presence of phosphate anion Absence of phosphate anion
3. EXAMINATION OF ANIONS IN SOLUTION PREPARATION OF SODIUM CARBONATE EXTRACT			
	A small amount of the given mixture and sodium carbonate salt are taken in the ratio of 1:3 in a clean conical flask and a test tube full of distilled water is added to it. Then the content is boiled for 5 minutes and filtered in a test tube to get the extract. The extract is divided into several portions and the following tests are carried out.		
(I)	PRECIPITATION OF SILVER SALT A portion of the extract is neutralized with dilute HNO_3 added dropwise with shaking till the effervescence ceases and centrifuged. To the centrifugate, a few drops of silver nitrate reagent are added and centrifuged.	a) A curdy-white precipitate appears, dissolves readily in aqueous ammonia and represcipitates with dilute HNO_3 $Cl^- + AgNO_3 \rightarrow NO_3^- + AgCl$ (curdy-white precipitate) b) A pale-yellow precipitate appears, dissolves readily in aqueous ammonia and reprecipitates with dilute HNO_3 $Br^- + AgNO_3 \rightarrow NO_3^- + Ag\ Br$ (Pale-yellow precipitate)	May be chloride anion Presence of Bromide Anion
	To the centrifugate, aqueous Ammonia is added gradually, along the sides of the test tube without shaking.	a) Yellow ring appears at the junction of solutions, soluble in NH_4OH and in dilute $HNO_3 \rightarrow PO_4^{3-} + 3\ AgNO_3\ \ 3\ NO_3 +$ $Ag_3\ PO_4$ (Yellow ring) b) No characteristic reaction	Presence of phosphate Absence of chloride, bromide, and phosphate anions

ii)	PRECIPITATION OF BARIUM SALTS A portion of the extract is neutralized with dilute HCl, added dropwise with shaking till the effervescence ceases and centrifuged. To the centrifugate, a few drops of Barium chloride are added and centrifuged.	a) White precipitate appears, insoluble in hot dilute HCl and dilute HNO_3 $SO_4^{2-} + BaCl_2 \rightarrow 2\ Cl^- + BaSO_4$ (white precipitate) b) No white precipitate appears	Presence sulphate anion Absence of sulphate Anion
	To the centrifugate, aqueous ammonia is added and centrifuged again	a) White precipitate appears and dissolves in dilute acetic acid b) While precipitate appears and found insoluble in dilute acetic acid c) No characteristic reaction	Presence of phosphate or borate anion Presence of oxalate or fluoride anion Absence of phosphate, borate, oxalate and fluoride anion
iii)	PRECIPITATION OF LEAD SALT A portion of the extract is neutralized with dilute acetic acid, added dropwise with shaking till the effervesence ceases and centrifuged. To the centrifugate, a few dorps of lead and acetate solution are added and centrifuged.	a) A white precipitate appears, dissolves readily in ammonium acetate anion $SO_{3_{2-}} + Pb(Oac)_2 \rightarrow 2\ OAc^- + Pb\ SO_4$ (white precipitaate) b) No characteristic reaction	Presence of sulphate anion Absence of sulphate anion
iv)	PRECIPTATION OF CALCIUM SALTS A portion of the extract is neutralized with dilute acetic acid added drop wise with shaking till the effervescence ceases and centrifuged. To the centrifuge a few drops of calcium chloride solution are added and centrifuged. To the residue 2 drops of dilute H_2SO_4 and a dorp of very dilute $kmNO_4$ are added.	a) White precipitate, does not decolourise pink colour of $KMnO_4$ solution, soluble in HOAc $F^- + CaCl_2 \rightarrow 2\ Cl^- + Ca\ F_2$ (white precipitate) b) White precipitate, decolourises pink colour of $KMnO_4$ solution $(COO)_2^{2-} + CaCl_2 \rightarrow 2Cl^- + Ca(COO)_2$ (white precipitate) c) No characteristic reaction	Presence of fluoride anion Presence of oxalate anion Absence of fluoride and oxalate anions
v)	BROWN RING TEST		Presence of nitrate anion

	A portion of the extract neutrialized with dilute H_2SO_4 added dropwise with shaking till the effervesence ceases and a freshly prepared solution of ferrous sulhate is added without shaking. Then a drop of conc H_2SO_4 is added along the side of the test tube	a) A brown ring appears at the junction of the 2 layers $NO_3^- + H^+ \rightarrow HNO_3$ $Fe^{2+} + NO_3^- + 4H^+ \rightarrow Fe^{3+} + 2H_2O + NO$ $FeSO_4 + NO + 5H_2O \rightarrow$ $[Fe(H_2O)_3NO]SO_4$ (brown ring) b)No brown ring appears	Absence of nitrate anion

SYSTEMATIC ANALYSIS FOR CATIONS:

IN SOLUTION ELIMINATION OF INTERFERING ANIONS

Interfering anions are anions which cause precipitation of cations outside their normal groups. Salts of such anions are soluble in mineral acids, but are insoluble in neutral or alkaline solution. Since dilute HCl is the group reagent evolved for the analysis of groups I and II, interfering anions will not affect the analysis of group I and II cations.

Since aqueous ammonia (base) is the group reagent involved for the analysis of group III, interfering anions will cause the precipitation of not only group III cations, but also the cations of group IV, V and VI.

So, it is essential to eliminate the interfering anions, before entering into the systematic analysis of cations

ELIMINATION OF INTERFEREING OXALATE ANION

A little of the given unknown mixture is roasted for 15 minutes in a china dish. The residue is used for group separation analysis.

ELIMINATION OF INTERFERING FLUORIDE OR BORATE ANION

A little of the given unknown mixture is heated in a china dish with 1 cc of conc. HCl to dryness. The process is repeated 4 to 5 times. The final residue is utilized for group separation analysis.

$F^- + H^+ \rightarrow HF$

$BO_{3-}^{3} + 3H_+ \rightarrow HBO_3$

ELIMINATION OF INTERFERING PHOSPHATE ANION

Elimination of phosphate anion is to be done at the beginning of group III analysis. The residue for group III contains actually phosphates of non-group III cations as well. The centrifugate from group II is boiled well, to expel all hydrogen sulphide and a drop of conc. HNO_3 acid is added and boiled gently. Then a few drops of ammonium chloride solution and 1 ml of zirconyl chloride reagent are added and digested for 2 minutes it is centrifuged and the centrifugate is tested for the presence of phosphate anion by adding zirconyl chloride reagent again. The same process is repeated till all phosphate has bean precipitated and this residue of zirconium phosphate is rejected. The centrifugate is used for group separation analysis from group III.

<table>
<tr><td colspan="5">A small amount of the given unknown mixture is made to dissolve in a suitable solvent like dilute or conc. HCl or H_2SO_4or HNO_{3-} to this solution, group I reagent, namely dilute HCl is added to slight excess, for complete precipitation and centrifuged. Pb^{2+}+2 HCl $\rightarrow$ 2 H+ + Pb Cl_2 group I precipitate)</td></tr>
<tr><td>RESIDUE
Presence of group I cation $PbCl_2$</td><td colspan="4">CENTRIFUGATE for group II analysis
To the centrifugate, group II reagent namely hydrogen sulphide gas passed to saturation and centrifuged.
$Cu^{2+} + H_2S \rightarrow 2\ H^+ + Cu\ S$ (black precipitate for group II)
$Bi^{3+} + 3\ H_2S \rightarrow 6H^+ + Bi_2\ S_3$ (precipitate for group II)
$Cd^{2+} + H_2S \rightarrow 2H^+ + Cd\ S$ (precipitate for group II)</td></tr>
<tr><td>NO RESIDUE
Absence of Group I cation</td><td>RESIDUE
Presence of group II cations
Cu S or $Bi_2\ S_3$ or Cd S
NO RESIDUE
Absence of Group II cations</td><td colspan="3">CENTRIFUGATE (for group III analysis)
The centrifugate is boiled to expel all excess of hydrogen sulphide gas and a drop of HNO_3 is added and boiled for sometime. Then group III reagents namely ammonium chloride solution and aqueous ammonia (slight excess0 are added and centrifuged.
$Mn^{2+} + 2\ NH_4\ OH \rightarrow 2\ NH_4^+ + Mn\ (OH)_2$
$Co^{2+} + H_2S \rightarrow 2\ H^+ + CoS$
$Zn^{2+} + H_2S \rightarrow 2\ H^+ + Zn\ S$ (precipitate for group IV)
$Ni^2 + H_2S \rightarrow 2\ H^+ + Ni\ S$</td></tr>
<tr><td></td><td></td><td>RESIDUE
Presence of group IV cations
Mn S, CO S,Zn S
and Ni S
NO RESIDUE
Absence of group IV cations</td><td colspan="2">CENTRIFUGATE (for group V analysis)
The centrifugate is boiled to expel all excess of hydrogen sulphide gas and a few drops of dilute HNO_3 of dilute HNO_3 are added and again boiled to concentrate the solution. Then group v reagent namely ammonium carbonate solution is added for complete precipitation and centrifugate.
$Ca^{2+}{}_+ (NH_4)_2CO_3 \rightarrow 2\ NH_4^+ + CaCO_3$
$Ba^{2+} - (NH_4)_2CO_3 \rightarrow 2\ NH_4^+ + Ba\ CO_3$ (group IV precipitate)
$S_1^{2-} + (NH_4)_2CO_3 \rightarrow 2\ NH_4 + SrCO_3$</td></tr>
<tr><td></td><td></td><td></td><td>RESIDUE
Presence of group V cations
Ca Co_3, Ba CO_3 and Sr CO_3
NO RESIDUE</td><td>CENTRIFUGATE (for group VI analysis)
The centrifugate is used for the analysis of group VI cations</td></tr>
</table>

			Absence of group V cation	

ANALYSIS OF GROUP I CATIONS

<table>
<tr><td colspan="2">The residue for group I is washed with water and boiled for sometime and centrifuged</td></tr>
<tr><td>NO RESIDUE
Absence of
Mercury and
silver cations</td><td>CENTRIFUGATE :
1. To one portion of the centrifugate, potassium chromate solutions is added
A yellow precipitate appears; presence of lead cation
$Pb Cl_2 + K_2CrO_4 \rightarrow 2K Cl + Pb CrO_4$(Yellow)
No yellow precipitate appears
Absence of lead cation
2. To the second portion of the centrifugate, potassium iodide solution is added $PbCl_2 + 2 KI \rightarrow 2KCl+PbI_2$ (golden spangles)
A yellow precipitate appears It is boiled with water to dissolve and cooled under tap water
Golden spangles appear
Presence of lead cation $Pb Cl_2 + 2 K Cl \rightarrow Pb I_2$
No golden spangles appear
Absence of lead cation</td></tr>
</table>

ANALYSIS OF GROUP II CATIONS

<table>
<tr><td colspan="3">The residue for group II is washed with water to remove alkali and the washings are discarded. Then a few drops of dilute HNO_3 are added and boiled. Then a few drops of dilute H_2SO_4 are added and centrifuged.
CuS or Cd S or $Bi_2S_3 + HNO_3 \rightarrow$ Soluble nitrate of group II cations</td></tr>
<tr><td>NO RESIDUE
Absence of
Mercury and
Lead cations</td><td colspan="2">CENTRIFUGATE:
To the centrifugate, aqueous ammonia is added in drops to slight excess, heated and centrifuged
Nitrates of group II cations + $NH_4OH \rightarrow [Cu(NH_3)_4]^{2+}$ aqueous + $[Cd(NH_3)_4]^{2+}$ aqueous + $Bi(OH)_3$ residue.</td></tr>
<tr><td></td><td colspan="2"></td></tr>
<tr><td></td><td>RESIDUE
It is dissolved by adding dilute HCl and divided into two portions. $Bi(OH)_3 + 3 HCl \rightarrow 3 H_2O + BiCl_3$</td><td>CENTRIFUGATE
To the centrifugate, dilute H_2SO_4 is added followed by hydrogen sulphide gas. The precipitate is heated with a few drops of conc. HCl and again H_2S gas is passed and centrifuged
$Cu SO_4 + H_2S \rightarrow H_2SO_4 + Cu S$ (black precipitate)</td></tr>
</table>

	To the first portion, a few drops of sodium hydroxide and sodium stannite solution are added. $2\ Bi^{3+} + 6\ OH^- + 3\ Na_2\ SnO_2 \rightarrow$ $3\ Na_2\ SnO_3 + 3\ H_2O + 2\ Bi$ (black ppt.) Black and white precipitate appears Presence of Bismuth cation. To the second portion, a slight excess of water is added $Bi^{3+} + 3\ H_2O \rightarrow 6H + Bi(OH)_3$ precipitate White turbidity appears. Presence of Bismuth cation	RESIDUE The black residue is dissolved in drops of dilute HNO_3 and 3 props of dilute acetic acid are added. Then potassium ferrocyanide solution is added. $Cu\ S + 2\ HNO_3 \rightarrow 2\ H^+ + Cu(NO_3)_2$ $Cu^{2+} + 2\ OH^- \rightarrow Cu(OH)_2$ (blue) $Cu^{2+} + K_4\ [Fe(CN)_6]$ $\rightarrow Cu^{2+}[Fe(Cn)_6]$ (red) Reddish-brown Precipitate appears Presence of copper cation No precipitate appears Absence of copper cation	CENTRIFUGATE The centrifugate is diluted with water and hydrogen sulphide is passed $Cd^{2+} + H_2S \rightarrow 2\ H^+ + Cd\ S$ (yellow precipitate) Yellow precipitate appears Presence of cadmium cation No precipitate appears Absence of cadmium cation

ANALYSIS OF GROUP III CATIONS

The residue for group III cations is washed with water and boiled with a little of sodium peroxide solid. It is stirred and boiled for some more time and centrifuged. Mn^{2+} or Fe^{2+} or $Al^{3+} + Na_2O_2 \rightarrow Na_3\,[Al(OH)_6]$ (in centrifugate)

RESIDUE:

The residue is dissolved dilute HCl and divided into two parents
To the first portion ammonium thiocyanate solution is added
$Fe(OH)_3 + 3\,HCl \rightarrow Fe\,Cl_3 + 3\,H_2O$
$Fe^{3+} + 3\,NH_4\,CNS \rightarrow 3NH_4Cl + Fe(CNS)$ (bloodred colour)

Blood-red colour appears
Presence of iron cation

No colour appears
Absence of iron cation

To the second portion, potassium ferrocyanide solution is added
$FeCl_3 + K_4\,[Fe(CN)_2 \rightarrow 3Cl^- + K\,Fe[Fe(CN)_6]$ (Prussian blue)

Blue colour appears
Presence of iron cation

No blue colour appears
Absence of iron cation

CENTRIFUGATE:

It is divided into two portions
The first portion is boiled with solid ammonium chloride
$Al^{3+} + 3\,NH_4OH \rightarrow 3\,NH_4^+ + Al(OH)_3$ (gelatinous precipitate)

Gelatinous white precipitate appears
Presence of aluminium cation

2. To the second portion, dilute HCl is added followed by aluminon reagent and aqueous ammonia
$Na_2\,[Al(OH)_6] + 6HCl \rightarrow 3\,Na\,Cl + 6H_2O + Al\,Cl_3$
$Al\,Cl_3 + 3\,NH_4\,OH \rightarrow 3\,NH_4Cl + Al(OH)_3$
This $Al(OH)_3$ absorbs the coloring matter and forms red-lake

Red-lake appears
Presence of aluminum cation

No characteristic reaction
Absence of aluminum cation

ANALYSIS OF GROUP IV CATIONS

The residue for group IV cations, is washed with water and digested with a little of dilute HCl acid and centrifuged
Zn S and Mn S are soluble in dilute HCl and they are percent in the centrifugate, leaving CoS and NiS residue

RESIDUE

The residue containing CoS and NiS is dissolved in least quantity of conc. HNO_3. It is evaporated just to dryness. The final residue is dissolved in 1 ml of water and divided into 3 portions.

To the first portion, a few drops of ammonium thiocyanate and amyl alcohol are added and shaken well.

$COCl_2 + 4\,NH_4CNS \rightarrow 2\,NH_4Cl + (NH_4)_2[Co(CNS)_4]$ [deep blue complex]

Blue layer appears
Presence of cobalt cation

To the second portion, ammonium chloride, ammonium hydroxide and potassium ferricyanide solutions are added one by one.

$CoCl_2 + K_3[Fe(CN)_6] \rightarrow CO(CN)_2$ [reddish-brwn precipitate]

Reddish brown precipitate appears
Presence of cobalt cation

To the third portion, ethanol, DMG and aqueous ammonium hydroxide solution are added

Rosy Read percipitate or colour is formed. Person of nickel cation

CENTRIGUGATE

It is boiled to expel hydrogen sulphide gas and sodium hydroxide is added in excess. Then it is centrifuged.

$Zn\,Cl_2 + 4\,NaOH \rightarrow Na_3[Zn(OH)_4] + 2\,Na\,Cl$

$Mn\,Cl_2 + 2\,NaOH \rightarrow Mn(OH)_2 + 2Na\,Cl$

RESIDUE

It is dissolved in 1 ml of dilute HNO_3 and divided into two portion

To the first portion sodium bismuthate is added stirred and centrifuged.

Pink colour appears
Presence of Mn cation

2. To the second portion a pinch of Lead dioxide is added, boiled and allowed to stand

Pink colour appears
Presence of Mn cation

CENTRIFUGATE

It is divided into two portions

To the first portion, hydrogen sulphide gas is passed

$Na_3[Zn(OH)_4] + 2H_2S \rightarrow Na_2S + 4\,H_2O + Zn\,S$

Dirty white precipitate appears

It is dissolved in conc. HNO_3 after removing H_2S and cobalt nitrate solution is added. A strip of filter paper is dipped in the solution and burnt to an ash.

Green ash appears .
Presence of Zn cation

2. To the second portion, a few drops of dilute HOAc are added followed by potassium ferrocyanide.

$Na_2[Zn(OH)_4] + 4\,HOAc \rightarrow Zn(OAc)_2 + 2Na\,OAc + 4\,H_2O$

$2\,Zn(OAc)_2 + K_4[Fe(CN)_6] \rightarrow 4\,K\,OAc + Zn_2Fe(CN)_6]$

[dirty white precipitate]

Dirty white precipitate appears
Presence of Zinc cation.

ANALYSIS OF GROUP V CATIONS

The residue for group V cations, is washed with water and dissolved in minimum quantity of dilute acetic acid and 1 ml of potassium chromate is added for complete precipitation and centrifuged. [carbonates of barium, strontium and calcium)

$MCO_3 + 2\ HOAc \rightarrow M(OAc)_2 + CO_2 + H_2O$

$Ba(OAc)_2 + K_2\ CrO_4 \rightarrow 2\ K\ OAc + Ba\ CrO_4$ (precipitated leaving the carbonates of Sr and Ca in centrifugate)

RESIDUE

Yellow residue is mixed with a drop of conc. HCl and made as a paste. The paste is introduced at the base of the outer oxidizing region of the non –luminous flame of burner.

Green Flame appears
Presence of barium cation

No Flame appears
Absene of barium cation

CENTRIFUGATE:

The centrifugate is neutralized with aqueous ammonia and ammnium carbonate is added and centrifuged. The residue is dissolved in dilute acetic acid and divided into two portions.

1. To the first portion, 1 ml of conc. H_2SO_4 are added.

$Sr\ CO_3 + H_2SO_4 \rightarrow Sr\ SO_4$

White precipitate appears
Presence of stronium cation

2. To the second poriton, satruated solution of ammonium sulphate is added and centrifuged. To the centrifugate, 1 ml of HOAc and ammonium oxalate solutions are added followed by aqueous ammonia

$CaCO_3 + (NH_4)_2\ SO_4 \rightarrow (NH_4)\ CO_3 + Ca\ SO_4$

$Ca\ SO_4 + 2\ HOAc \rightarrow H_2SO_4 + Ca\ (OAc)_2$

$Ca(OAc)_2 + (NH_4)\ C_2\ O_4 \rightarrow 2NH_4\ OAc + CaC_2\ O_4$

White precipitate appears
Presence of calcium cation

No white precipitate appears
Absence of calcium cation

ANALYSIS OF GROUP VI CATIONS

The centrifugate from group V is divided into two portions

1. To the first portion ammonium chloride solution and aqueous ammonia are added followed by the addition of sodium hydrogen phosphate reagent. The sides of the test tube is scratched with a glass rod.

$Mg^{2+} + Na_2\ H\ PO_4 + NH_3 \rightarrow 2\ Na^+ + Mg\ NH_4PO_4$ (white precipitate)

White precipitate appears
Presence of magnesium cation

No white precipitate appears
Absence of magnesium cation

2. To the second portion a few drops of dilute HCl are added, stirred and a drop of Magneson reagent is added. Then a few drops of sodium hydroxide are added.

White precipitate appears
Presence of magnesium cation

No blue precipitate appears
Absence of Magnesium cation

TEST FOR AMMONIUM CATION

Since many ammonium salts are added during the course of analysis ammonium cation has to be tested in the unknown before proceeding to the systematic analysis for cations.

The given unknown mixture is washed with water and centrifuged.

To the centrifugate, a few drops of Nessler's reagent are added followed by the addition of sodium hydroxide solution

A brown precipitate appears Presence of ammonium cation	No brown precipitate appears Absence of ammonium cation

REPORT The given unknown mixture contians the following anions and cation

ANIONS: (I) Non interfering_____ CATIONS (1)_____(Group_____)

(II) Interfering _____ (2)_____(Group_____)