UNIT 6 DETECTION OF THE CATIONS-II

Structure

6.1 INTRODUCTION

In the preceding unit, you studied the concepts of solubility, solubility product, the common ion effect and complex formation. You also studied that the cations are classified into seven analytical groups on the basis of similarities in the solubility behaviour of their sparingly soluble salts and also on the basis of similarities in their chemical behaviour. Also that the cations of each analytical group are separated from those of others by selective precipitation. The cations of individual groups are then separated from each other by selective dissolution of their precipitates and are identified by specific confirmatory tests. In this unit, you will study the details of the scheme of analysis and the chemistry of separation and identification of cations present in a mixture.

Objectives

After studying this unit, you should be able to:

- classify the cations into analytical groups,
- list the cations of each analytical group,
- separate cations into analytical groups by selective precipitation,
- identify the cations present in a mixture by performing the systematic tests for cations,
- discuss the chemistry of analysis of cations,

- write down the colour and the chemical formulae of the precipitate formed by each cation on reaction with group reagent, and
- if possible, perform the flame tests for certain cations present in the mixture.

6.2 PRELIMINARY INVESTIGATION OF THE SAMPLE

Observe the colour of the sample and the solution. It may provide a clue to the identity of cations and may help in performing subsequent successful analysis of the sample. The colours of some of the cations are listed below.

Cu^{2+}	blue green
Ni^{2+}	green
Mn^{2+}	faint pink (above 0.5 M)
Co^{2+}	pink-red
Cr^{3+}	violet-purple
Fe^{2+}	pale green
Fe^{3+}	yellow

The solution may acquire purple (MnO_4^-), pale green (CrO_4^{2-}) or orange ($Cr_2O_7^{2-}$) colour due to the presence of anions listed in the parenthesis.

Sometimes the colour of the solution may not represent the true identity of the ions because of the presence of more than one species. The concentration of the ion in solution is also very important. For example, an aqueous solution of Mn^{2+} salts may appear almost colourless unless present in a concentration above 0.5 M. Incidentally cobalt(II) salts are also pink. The presence of a complexing anion has also an important influence on the colour of the cations in solution. In the presence of high concentration of chloride ions, a cobalt salt in solution may appear deep blue in colour. Likewise, nickel(II) and copper(II) salts may appear either blue or green depending on the anion present. Iron(II) salts though generally pale green may appear almost colourless in aqueous solution. The observations with regard to the presence of coloured cations, therefore, may not be conclusive.

6.3 PREPARATION OF SOLUTION FOR THE ANALYSIS OF CATIONS

Aqua regia consists of 3 parts of concentrated hydrochloric acid for every 1 part of concentrated nitric acid.

Cations are separated into analytical groups by selective precipitation as sparingly soluble salts from aqueous solution. Therefore, first of all the solid mixture should be brought into solution. Place 100 mg of the finely powdered material in a glass test tube and add the solvents in the following order:

i) distilled water
ii) dilute HCl (6 M)
iii) concentrated HCl (12 M)
iv) dilute nitric acid (6 M)
v) concentrated nitric acid (16 M)
vi) aqua regia

Treat the sample first with distilled water. If the substance does not dissolve completely, keep in a boiling water bath for nearly 10 minutes and stir periodically. If the sample dissolves completely stop adding distilled water. If the substance does not dissolve completely, treat the residue with dilute hydrochloric acid and heat gently. If a solid still remains, try dissolution in concentrated hydrochloric acid and proceed as before.

If a residue still remains, try dissolution in dilute nitric acid and then concentrated nitric acid. If the sample dissolves in any of the solvents, there is no need to test with the other solvents.

If the substance still does not dissolve in any of the solvents completely, add aqua regia and heat to near dryness in a china dish. Note the colour change, odour and colour of the gases evolved. This may sometimes be quite useful in the analysis of ions present in the substance.

Always drive off the volatile acid and carefully evaporate the solution to nearly 0.5 – 1.0 cm^3. Do not evaporate the solution to dryness as insoluble oxides may form, which are subsequently difficult to dissolve. Extract with a small volume of distilled water and add dilute hydrochloric acid before proceeding for cation analysis.

Use 500 mg to 1.0 g of the sample in a china dish or small beaker after making a proper choice of the solvent and proceed in the manner as described above for complete dissolution of the sample.

Water is a preferred solvent for most of the ionic substances. Many inorganic compounds which contain anions of weak acids are insoluble in water. These compounds are soluble in dilute strong acids like hydrochloric acid (6 M). Carbonates, sulphites, oxalates, borates, thiosulphates are soluble in dilute solutions of strong acids.

A concentrated solution of a non-oxidising strong acid such as hydrochloric acid (12 M) often provides a rich source of hydronium ions. Such a treatment may be necessary when the anion is derived from a strong acid.

Oxidising acid, like nitric acid attacks substances when hot and oxidises them. Finally when every other acid fails, aqua regia generally dissolves compounds because of its oxidising action or due to the formation of chloro complexes. All sulphides are soluble in aqua regia. Hot dilute nitric acid dissolves all the sulphides except HgS.

If still a residue remains, consult your Counsellor.

6.4 SEPARATION OF THE CATIONS INTO ANALYTICAL GROUPS

The cations of each successive group are precipitated as sparingly soluble compounds with anions supplied by the group reagents. The precipitate containing cations of one group is separated either by filtration or centrifugation. The centrifugate or solution remaining after filtration is similarly converted into a sparingly soluble precipitate by another group reagent. However, care must be taken that precipitation is complete before proceeding for the next group. Always add a slight excess of the precipitating agent to ensure complete precipitation.

The major classification of the analytical groups is as follows:

Cations of Analytical Group I: Pb^{2+}, Ag^{2+} and Hg_2^{2+}

These are precipitated as chlorides since the chlorides of Ag(I), Hg(I) and Pb(II) only are insoluble in the presence of 0.2 M HCl solution, other cations remain in solution since the chlorides of other cations being soluble.

Cations of Analytical Group II : Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{4+}

These are precipitated as sulphides from a solution of lower pH made 0.3 M in HCl and saturating the solution with H_2S or using H_2S water. These cations precipitate as sulphides from solution of high H^+ ion concentration and require a low concentration of S^{2-} ions because the sulphides of these cations have very low solubility, i.e., the sulphides of the group are those with the smallest K_{sp} values. Therefore, they precipitate in the presence of sulphide ion concentration that is kept low enough to avoid precipitation of the more soluble sulphides of the cations of Group IV. The solution should, however, be diluted atleast 100 times and hydrogen sulphides should be passed before proceeding to the next group otherwise Cd^{2+} is likely to be missed. This group is further separated into subgroups by using yellow ammonium sulphide.

Cations of Analytical Group III : Fe^{3+}, Cr^{3+}, Al^{3+}

After boiling off H_2S, and oxidation of Fe^{2+}, these cations are precipitated as hydroxides by controlling the concentration of OH^- ions by addition of NH_4OH in the presence of NH_4Cl. All other cations remain in solution.

Cations of Analytical Group IV : Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}

The sulphides of cations of this group are more soluble than the sulphides of the cations of Group II. The cations of this group obviously require a higher concentration of S^{2-} ions, which is achieved by raising the pH in the presence of NH_4Cl–NH_4OH buffer solution, for precipitation to occur. All other cations of higher groups remain in solution.

Cations of Analytical Group V : Ba^{2+}, Sr^{2+}, Ca^{2+}

These cations are precipitated after boiling off H_2S and precipitating with ammonium carbonate in the presence of NH_4Cl and NH_4OH. Other cations remain in solution. This group is sometimes referred to as the 'insoluble carbonate group'.

Cation of Analytical Group VI: Mg^{2+}

Mg^{2+} belongs to this group which is precipitated as $Mg(NH_4)PO_4$ by the addition of $(NH_4)_2HPO_4$ in buffered aqueous ammonia solution.

Cations of Analytical Group Zero: NH_4^+, K^+ and Na^{2+}

Salts of Na^+, NH_4^+ and K^+ are soluble in water. Therefore, these cations are sometimes referred to as cations belonging to the soluble group. They are generally analysed before proceeding for the analysis of cations of Group I and therefore, are known as the cations of Group zero also.

This procedure divides the cations present in original mixture into various groups. Each group is then separated into individual ions, which are subjected to confirmatory tests.

The separation of cations into different analytical groups along with the group reagents, formulae and colours of the precipitates is given in Table 6.1. The procedure for separating the cations into analytical groups is summarised in Flow Chart 6.1.

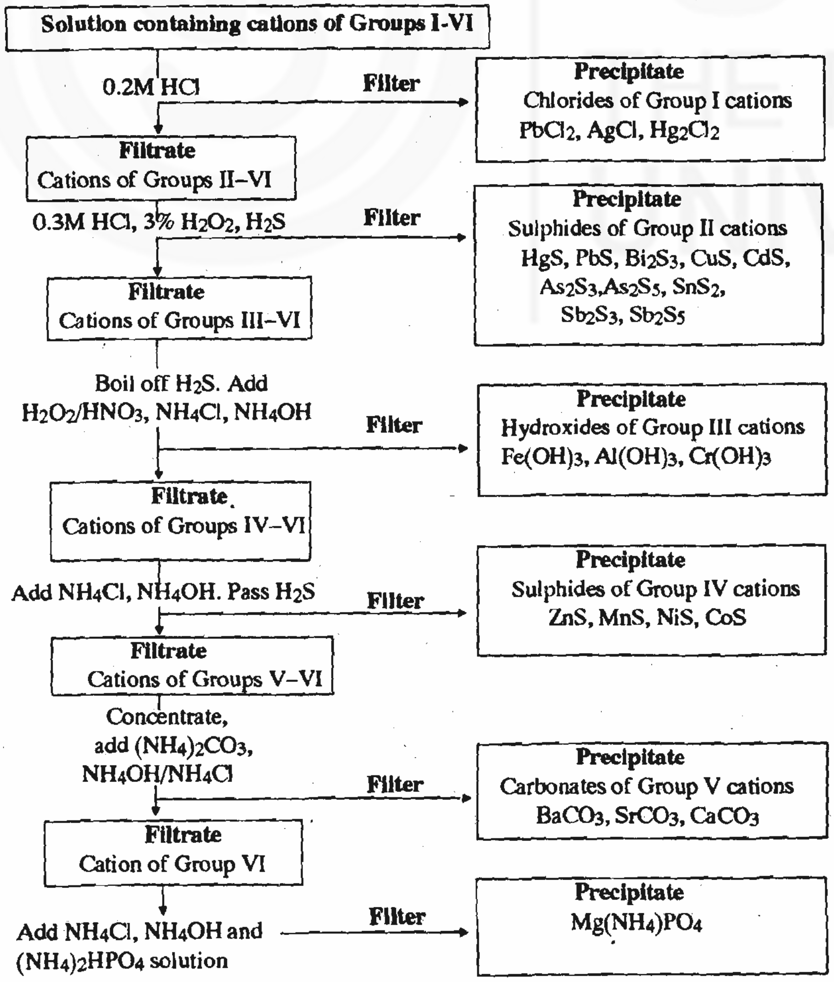
6.5 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP I

The cations of Group I are Pb^{2+}, Ag^+ and Hg_2^{2+}. The Group I cations are precipitated as chlorides. The K_{sp} values for $AgCl$ and Hg_2Cl_2 are very small, while the K_{sp} for $PbCl_2$ is rather large. If enough hydrochloric acid is added to the aqueous solution

Table 6.1 : Separation of Cations into Analytical Groups

Analytical group	Group reagent	Ion	Product
I	0.2 M HCl	Pb(II)	$PbCl_2$ (white)
		Ag(I)	AgCl (white)
		Hg(I)	Hg_2Cl_2 (white)
II	0.3 M HCl, +H_2S	Hg(II)	HgS (black)
		Pb(II)	PbS (deep brown)
		Bi(III)	Bi_2S_3 (black)
		Cu(II)	CuS (black)
		Cd(II)	CdS (yellow)
		As(III)	As_2S_3 (yellow)
		As(V)	As_2S_5 (yellow)
		Sb(III)	Sb_2S_3 (orange)
		Sb(V)	Sb_2S_5 (orange)
		Sn(IV)	SnS_2 (yellow)
III	NH_4OH/NH_4Cl	Fe(III)	$Fe(OH)_3$ (brown)
		Al(III)	$Al(OH)_3$ (white)
		Cr(III)	$Cr(OH)_3$(gray blue)
IV	NH_4OH/NH_4Cl, H_2S	Co(II)	CoS (black)
		Ni(II)	NiS (black)
		Mn(II)	MnS (pink)
		Zn(II)	ZnS (white)
V	NH_4OH/NH_4Cl, $(NH_4)_2CO_3$	Ba(II)	$BaCO_3$ (white)
		Sr(II)	$SrCO_3$ (white)
		Ca(II)	$CaCO_3$ (white)
VI	$(NH_4)_2HPO_4$, NH_4OH/NH_4Cl	Mg(II)	$Mg(NH_4)PO_4$ (white)
Zero	None	NH_4^+, K^+, Na^+	–

Flow Chart 6.1 : Separation of Cations into Analytical Groups



of these ions so as to raise the [Cl^-] to 0.2 M, very few Ag^+ or Hg_2^{2+} ions will remain in solution. The presence of hydrogen ion prevents the precipitation of the bismuth and the antimony oxychlorides, which would form in the absence of these ions:

$$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$$

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

$$Hg_2^{2+}(aq) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s)$$

$$Bi^{3}(aq) + Cl^-(aq) + H_2O(l) \rightleftharpoons BiOCl(s) + 2H^+(aq)$$

$$Sb^{3}(aq)+ + Cl^-(aq) + H_2O(l) \rightleftharpoons SbOCl(s) + 2H^+(aq)$$

A very large excess of the acid will contain an equally large excess of chloride ions. Silver and lead chlorides form soluble chloro complexes in the presence of a large excess of chloride ions. One consequence of chloro complex formation is that excess of chloride ions will cause this group precipitate to redissolve. Mercury(I) chloride does not dissolve because the chloro complexes of mercury(I) are unstable.

$$Ag^+(aq) + 2Cl^-(aq) \rightleftharpoons [AgCl_2]^-(aq)$$

$$Pb^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [PbCl_4]^{2-}(aq)$$

A second consequence can be the formation of stable chloro complexes of some other cations, such as $[CdCl_4]^{2-}$. Since $PbCl_2$ is several times more soluble than AgCl or Hg_2Cl_2, it is impossible to avoid carrying some of Pb(II) into the solution after separation of AgCl and Hg_2Cl_2. Consequently Group II of cation analysis always contains some Pb(II) ions.

Separation and Identification of Cations of Analytical Group I

Once the cations of this group are precipitated as chlorides, we need to separate the ions so that individual tests can be performed for the identification of individual ions.

Separation of lead(II) from other members is rather easy because the solubility of lead(II) chloride in hot water is several times greater than that at room temperature. This fact is made use of in the separation of lead from other cations of this group. [Solubility of $PbCl_2$: 9.9 g dm^{-3} at room temperature and 33.4 g dm^{-3} at 100°C]. Though the solubilities of chlorides of silver(I) and mercury(I) also increase with temperature, but the solubilities are so low that their ions are not detected by the method of qualitative analysis. [Solubility of AgCl: 0.089 mg dm^{-3} at 20°C and 0.21 mg dm^{-3} at 100°C; solubility of Hg_2Cl_2: 0.21 mg dm^{-3} at 20°C and 1.0 mg dm^{-3} at 45°C.]

The precipitate of Group I chlorides is boiled with water and filtered. The lead chloride passes into solution, whereas the silver chloride and mercury(I) chloride remain as solid.

$$PbCl_2(s) \xrightleftharpoons{\text{hot water}} Pb^{2+}(aq) + 2Cl^-(aq)$$

The hot filtrate deposits lead chloride on cooling. Consequently, the hot filtrate is used for confirmation of lead(II).

The precipitate of silver(I) and mercury(I) chlorides is thoroughly washed with hot water before addition of aqueous ammonia, otherwise a gray precipitate consisting of a mixture of basic lead(II) chloride, Pb(OH)Cl and lead(II) hydroxide, $Pb(OH)_2$ coats the precipitate of mercury(II) amido chloride, $HgNH_2Cl$.

$$PbCl_2(s) + NH_3(aq) + H_2O(l) \rightarrow Pb(OH)Cl(s) + Pb(OH)_2(s) + NH_4^+(aq) + 2Cl^-(aq)$$

Aqueous ammonia reacts with silver(I) chloride to form a colourless soluble ammine complex, $[Ag(NH_3)_2]^+$ while mercury(I) chloride undergoes disproportionation in the presence of excess ammonia solution to produce finely divided metallic mercury (black) and mercury(II) amidochloride (white) which stays as a precipitate.

$$Hg_2Cl_2(s) + 2NH_3(aq) \rightarrow Hg(l) + HgNH_2Cl(s) + NH_4^+(aq) + Cl^-(aq)$$

The black precipitate confirms that Hg(I) ions are present.

Identification of Lead(II)

Divide the hot solution of lead chloride into three parts and perform confirmatory tests for the presence of Pb(II).

i) Add potassium chromate when insoluble yellow $PbCrO_4$ is precipitated.

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$$

The precipitate of $PbCrO_4$ dissolves on addition of NaOH producing hydrogen plumbate(II) ion, $HPbO_2^-$. Lead chromate is reprecipitated when the solution is acidified with acetic acid as the excess hydroxide ion is neutralized and the equilibrium shifts to the left.

$$PbCrO_4(s) + 3OH^-(aq) \rightarrow HPbO_2^-(aq) + CrO_4^{2-}(aq) + H_2O(l)$$

ii) Add potassium iodide, when a yellow precipitate of PbI_2 forms. When this is warmed, the solution on cooling deposits crystals of PbI_2 as golden shining needles.

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$

iii) Add dilute sulphuric acid to the solution when a white precipitate of $PbSO_4$ is obtained. $PbSO_4$ dissolves in excess of acetate ions due to the formation of tetraacetatoplumbate(II) complex ion.

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$$

$$PbSO_4(s) + 4CH_3COO^-(aq) \rightleftharpoons [Pb(CH_3COO)_4]^{2-}(aq) + SO_4^{2-}(aq)$$

Lead sulphate is also soluble in excess of alkali hydroxide, when colourless $[Pb(OH)_4]^{2-}$ is formed.

$$PbSO_4(s) + 4OH^-(aq) \rightleftharpoons [Pb(OH)_4]^{2-}(aq) + SO_4^{2-}(aq)$$

Further confirmation can be obtained by acidification with acetic acid and adding K_2CrO_4 solution when a yellow precipitate of $PbCrO_4$ is formed.

$$[Pb(OH)_4]^{2-}(aq) + 4H^+(aq) \rightleftharpoons Pb^{2+}(aq) + 4H_2O(l)$$

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightleftharpoons PbCrO_4(s)$$

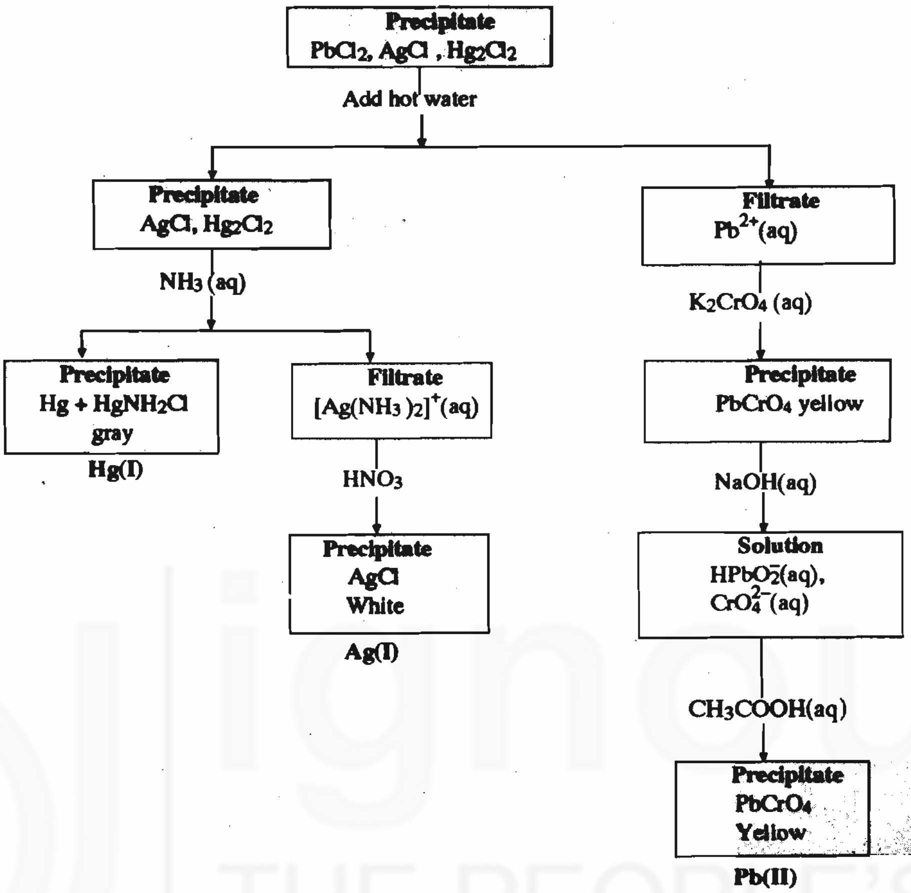
Identification of Silver(I)

The presence of Ag^+ ions in the colourless solution is confirmed by the acidification with dilute nitric acid when a white precipitate of silver(I) chloride is formed.

$$[Ag(NH_3)_2]^+(aq) + Cl^-(aq) + 2H^+(aq) \rightarrow AgCl(s) + 2NH_4^+(aq)$$

The nitric acid converts NH_3 to NH_4^+ thereby destroying the complex ion. This increases the concentration of free silver ions in the solution resulting into reprecipitation of AgCl. The procedure of analysis of the cations of Group I is summarised in Flow Chart 6.2.

Flow Chart 6.2 : Separation and Identification of Group I Cations



6.6 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP II

The cations of this group are Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{4+}. These cations of Group II are precipitated as sulphides from 0.3 M HCl solution saturated with H_2S. The sulphides of this group are the ones with the smallest K_{sp} values. At low pH, $[S^{2-}]$ is very low and only those cations which produce sparingly soluble sulphides with a very small K_{sp} will precipitate. Cations of other groups with relatively large K_{sp} values will not precipitate under these conditions. The key to the separation of cations of Group II and IV, therefore, lies in the difference between the K_{sp} values of sulphides of the cations of these groups. The real problem lies with the precipitation of CdS which has an intermediate K_{sp} value. Dilution of the solution decreases the concentration of H^+ ions and also releases Cd^{2+} from the $[CdCl_4]^{2-}$ complex. The slight increase in pH is enough to give a $[S^{2-}]$ sufficient to precipitate cadmium(II). Hydrogen peroxide is added to the solution to ensure oxidation of Sn(II) to Sn(IV) so that the much less soluble sulphide SnS_2 is produced.

$$Pb^{2+}(aq) + H_2S(aq) \rightarrow PbS(s) + 2H^+(aq)$$

$$Hg^{2+}(aq) + H_2S(aq) \rightarrow HgS(s) + 2H^+(aq)$$

$$2Bi^{3+}(aq) + 3H_2S(aq) \rightarrow Bi_2S_3(s) + 6H^+(aq)$$

$$\begin{aligned}
Cu^{2+}(aq) + H_2S(aq) &\rightarrow CuS + 2H^+(aq)\\
Cd^{2+}(aq) + H_2S(aq) &\rightarrow CdS(s) + 2H^+(aq)\\
2As^{3+}(aq) + 3H_2S(aq) &\rightarrow As_2S_3(s) + 6H^+(aq)\\
2Sb^{5+}(aq) + 5H_2S(aq) &\rightarrow Sb_2S_5(s) + 10H^+(aq)\\
Sn^{4+}(aq) + 2H_2S(aq) &\rightarrow SnS_2 + 4H^+(aq)\\
Sn^{2+}(aq) + H_2O_2(aq) + 2H^+(aq) &\rightarrow Sn^{4+}(aq) + 2H_2O(l)
\end{aligned}$$

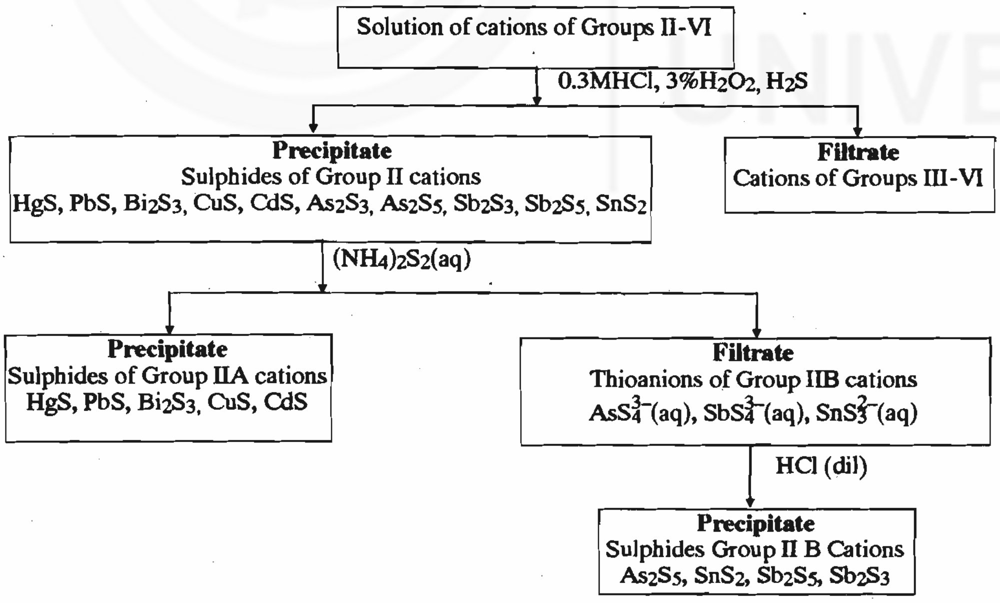
6.6.1 Separation of Analytical Group II into Group IIA and Group IIB

After precipitation the cations of Group II are separated into Group IIA and Group IIB by selective dissolution of the precipitate. The sulphides of arsenic, antimony and tin are separated from other members of the group by dissolving them in yellow ammonium sulphide.

$$\begin{aligned}
As_2S_3(s) + 4S_2^{2-}(aq) &\rightleftharpoons 2[AsS_4]^{3-}(aq) + S_3^{2-}(aq)\\
As_2S_5(s) + 6S_2^{2-}(aq) &\rightleftharpoons 2[AsS_4]^{3-}(aq) + 3S_3^{2-}(aq)\\
Sb_2S_3(s) + 4S_2^{2-}(aq) &\rightleftharpoons 2[SbS_4]^{3-}(aq) + S_3^{2-}(aq)\\
Sb_2S_5(s) + 6S_2^{2-}(aq) &\rightleftharpoons 2[SbS_4]^{3-}(aq) + 3S_3^{2-}(aq)\\
SnS_2(s) + 2S_2^{2-}(aq) &\rightleftharpoons [SnS_3]^{2-}(aq) + S_3^{2-}(aq)
\end{aligned}$$

The cations As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+} and Sn^{4+} constitute the Group IIB of the scheme. The sulphides of Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+} and Cd^{2+} do not dissolve in yellow ammonium sulphide and are left behind. These constitute the Group IIA of the scheme. The procedure for precipitation of Group II cations and their separation into Group IIA and Group IIB is summarised in Flow Chart 6.3.

Flow Chart 6.3 : Precipitation of Group II Cations and Separation into Group IIA and Group IIB



6.6.2 Separation of Cations of Group IIA

The separation of HgS from other members of this group is based on the solubility of PbS, Bi_2S_3, CuS and CdS in dilute HNO_3 while HgS remains insoluble.

$$3PbS(s) + 8H^+(aq) + 2NO_3^-(Aq) \rightarrow 3Pb^{2+}(aq) + 2NO(g) + 4H_2O(l) + 3S(s)$$

$$3CuS(s) + 8H^+(aq) + 2NO_3^-(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l) + 3S(s)$$

$$Bi_2S_3(s) + 4H^+(aq) + 2NO_3^-(aq) \rightarrow 2Bi^{3+}(aq) + 2NO(g) + 2H_2O(l) + 3S(s)$$

$$3CdS(s) + 8H^+(aq) + 2NO_3^-(aq) \rightarrow 3Cd^{2+}(aq) + 2NO(g) + 4H_2O(l) + 3S(s)$$

Mercury(II) sulphide dissolves in aqua regia due to the combined effect of very high oxidising action and complexing ability of aqua regia. This results in the formation of stable tetrachloromercurate(II) complex ion,$[HgCl_4]^{2-}$

$$3HgS(s) + 8H^+(aq) + 12Cl^-(aq) + 2NO_3^-(aq) \rightarrow 3[HgCl_4]^{2-}(aq) + 2NO(g) + 4H_2O(l) + 3S(s)$$

Lead(II) is separated from other members i.e., Cu(II), Cd(II), and Bi(III) by precipitation as $PbSO_4$. Nitric acid must be completely removed from the solution by fuming with concentrated H_2SO_4 since $PbSO_4$ is soluble in HNO_3. The evaporation must be carried out in a hood since the vapours of HNO_3, oxides of nitrogen and sulphur are extremely corrosive and toxic. The solution is diluted to reprecipitate $PbSO_4$.

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$$

Bismuth(III) is separated from the remaining members of the group, i.e., Cu(II) and Cd(II), by precipitation as $Bi(OH)_3$ by adding aqueous ammonia solution. Copper(II) and cadmium(II) stay in solution because they form tetraammine complexes, copper complex being deep blue in colour.

$$Bi^{3+}(aq) + 3NH_3(aq) + 3H_2O(l) \rightarrow Bi(OH)_3(s) + 3NH_4^+(aq)$$

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

$$Cd^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cd(NH_3)_4]^{2+}(aq)$$

The blue colour of the solution is a preliminary indication of the presence of Cu^{2+} ion.

6.6.3 Separation of Cations of Group IIB

The solution containing thioanions of arsenic, antimony and tin is acidified with dilute HCl. The sulphides of these cations are again precipitated along with sulphur in the colloidal form:

$$2[AsS_4]^{3-}(aq) + 6H^+(aq) \rightarrow As_2S_5(s) + 3H_2S(g)$$

$$2[SbS_4]^{3-}(aq) + 6H^+(aq) \rightarrow Sb_2S_5(s) + 3H_2S(s)$$

$$Sb_2S_5(s) \rightarrow Sb_2S_3(s) + S(s)$$

$$[SnS_3]^{2-}(aq) + 2H^+(aq) \rightarrow SnS_2(s) + H_2S(g)$$

$$S_2^{2-}(aq) + 2H^+(aq) \rightarrow H_2S(g) + S(s)$$

The separation of As_2S_5 from other members of this group is based on the dissolution of Sb_2S_3 and SnS_2 in concentrated HCl, due to the formation of tetrachloroantimonate(III) and hexachlorostannate(IV) ions:

$$Sb_2S_3(s) + 6H^+(aq) + 8Cl^-(aq) \rightarrow 2[SbCl_4]^-(aq) + 3H_2S(g)$$

$$SnS_2(s) + 4H^+(aq) + 6Cl^-(aq) \rightarrow [SnCl_6]^{2-}(aq) + 2H_2S(g)$$

The solution is boiled to expel H_2S and used to confirm the presence of antimony and tin ions in solution. The insoluble As_2S_5 is treated with aqueous ammonia and H_2O_2 or with nitric acid and the solution evaporated to near dryness. As a result arsenate ions are produced. Confirmation of arsenic is done using this solution.

$$As_2S_5(s) + 16NH_3(aq) + 20H_2O_2(aq) \rightarrow 2AsO_4^{3-}(aq) + 16NH_4^+(aq) + 5SO_4^{2-}(aq) + 12H_2O(l)$$

$$3As_2S_5(s) + 10H^+(aq) + 10NO_3^-(aq) + 4H_2O(l) \rightarrow 6H_3AsO_4(aq) + 10NO(g) + 15S(s)$$

The procedure for precipitation and separation of cations of Group II is summarised in Flow Chart 6.3.

6.6.4 Identification of the Cations of Group II

After separation of individual cations either by selective precipitation or by selective dissolution as discussed above, their presence is further confirmed by means of identification tests for each cation.

Identification of Mercury(II)

The precipitate of mercury(II) sulphide is black. Dissolve the precipitate in aqua regia and evaporate to near dryness. Add 1cm^3 conc. HCl and heat again. Dilute with water and divide into three parts.

i) Add a few drops of $SnCl_2$ solution to one part, appearance of a white precipitate which turns gray confirms mercury(II):

$$2Hg^{2+}(aq) + 2Cl^-(aq) + Sn^{2+}(aq) \rightarrow Hg_2Cl_2(s) + Sn^{4+}(aq)$$

$$Hg_2Cl_2(s) + Sn^{2+}(aq) \rightarrow 2Hg^0(l) + Sn^{4+}(aq) + 2Cl^-(aq)$$

ii) Add a few drops of KI solution to another part. A yellow precipitate of HgI_2 is formed. The precipitate dissolves on adding excess KI due to the formation of tetraiodomercurate(II), $[HgI_4]^{2-}$, complex ion:

$$Hg^{2+}(aq) + 2I^-(aq) \rightarrow HgI_2(s)$$

$$HgI_2(s) + 2I^-(aq) \rightarrow [HgI_4]^{2-}(aq)$$

iii) Add a small piece of copper wire to the third part, when a shining deposit of mercury is obtained on the copper wire and the solution turns greenish blue.

$$Hg^{2+}(aq) + Cu^0(s) \rightarrow Hg^0(l) + Cu^{2+}(aq)$$

Identification of Lead(II)

The precipitate of lead sulphate is white. Divide the precipitate into two parts and perform the following tests :

i) Heat one part of the precipitate with excess of ammonium acetate solution. The precipitate will dissolve due to the formation of tetraacetatoplumbate(II) complex ion:

$$PbSO_4(s) + 4CH_3COO^-(aq) \rightleftharpoons [Pb(CH_3COO)_4]^{2-}(aq) + SO_4^{2-}(aq)$$

ii) Heat the other part of the lead sulphate precipitate with excess of sodium hydroxide. The precipitate will dissolve to give a colourless solution due to the formation of tetrahydroxoplumbate(II) ion:

$$PbSO_4(s) + 4OH^-(aq) \rightleftharpoons [Pb(OH)_4]^{2-}(aq) + SO_4^{2-}(aq)$$

Acidify the solution with acetic acid and add potassium chromate solution. A yellow precipitate of lead chromate will be formed.

$$[Pb(OH)_4]^{2-}(aq) + 4H^+(aq) \rightleftharpoons Pb^{2+}(aq) + 4H_2O(l)$$

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$$

Identification of Bismuth(III)

The precipitate of $Bi(OH)_3$ is transparent and gelatinous. Confirm bismuth(III) by addition of a freshly prepared sodium tetrahydroxostannate(II) reagent (sodium stannite) to $Bi(OH)_3$ when black metallic bismuth precipitates.

$$2Bi(OH)_3(s) + 3[Sn(OH)_4]^{2-}(aq) \rightarrow 2Bi^\circ(s) + 3[Sn(OH)_6]^{2-}(aq)$$

Alternatively, dissolve $Bi(OH)_3$ in dilute HCl and divide into two parts.

$$Bi(OH)_3(s) + 3H^+(aq) \rightarrow Bi^{3+}(aq) + 3H_2O(l)$$

i) Add distilled water to one part when white bismuth oxychloride precipitates.

$$Bi^{3+}(aq) + Cl^-(aq) + H_2O(l) \rightarrow BiOCl(s) + 2H^+(aq)$$

ii) Add potassium iodide reagent dropwise to the second part when a black precipitate of BiI_3 is obtained. The precipitate dissolves readily in excess reagent when orange coloured tetraiodobismuthate ions are formed.

$$Bi^{3+}(aq) + 3I^-(aq) \rightarrow BiI_3(s)$$

$$BiI_3(s) + I^-(aq) \rightarrow [BiI_4]^-(aq)$$

Identification of Copper(II)

The presence of copper is confirmed by making the solution acidic with acetic acid and adding potassium hexacyanoferrate(II) when a reddish brown precipitate of $Cu_2[Fe(CN)_6]$ forms.

$$[Cu(NH_3)_4]^{2+}(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 4NH_4^+(aq)$$

$$2Cu^{2+}(aq) + [Fe(CN)_6]^{4-}(aq) \rightarrow Cu_2[Fe(CN)_6](s)$$

Cadmium ions under similar conditions produce a white precipitate.

$$2Cd^{2+}(aq) + [Fe(CN)_6]^{4-}(aq) \rightleftharpoons Cd_2[Fe(CN)_6](s)$$

When both copper(II) and cadmium(II) are present, copper ions are separated by reduction of the ammine complex with $Na_2S_2O_4$ (sodium dithionite). Under these conditions cadmium ions are not reduced and so after separation of metallic copper, the solution is saturated with H_2S when yellow CdS precipitates.

$$[Cu(NH_3)_4]^{2+}(aq) + S_2O_4^{2-}(aq) + 2H_2O(l) \rightarrow Cu^\circ(s) + 2SO_3^{2-}(aq) + 4NH_4^+(aq)$$

$$[Cd(NH_3)_4]^{2+}(aq) + S^{2-}(aq) \rightarrow CdS(s) + 4NH_3(aq)$$

Alternatively, acidify the solution containing Cu(II) and Cd(II) ions with dilute HCl and pass H_2S. Only black CuS precipitates. Separate the precipitate. Dilute the solution atleast 100 times and pass H_2S, a yellow precipitate of CdS will be formed:

$$[Cu(NH_3)_4]^{2+}(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 4NH_4^+(aq)$$

$$Cu^{2+}(aq) + H_2S(aq) \rightarrow CuS(s) + 2H^+(aq)$$

$$[Cd(NH_3)_4]^{2+}(aq) + 4H^+(aq) + 4Cl^-(aq) \rightleftharpoons [CdCl_4]^{2-}(aq) + 4NH_4^+(aq)$$

$$[CdCl_4]^{2-}(aq) \rightleftharpoons Cd^{2+}(aq) + 4Cl^-(aq)$$

$$Cd^{2+}(aq) + H_2S(aq) \rightleftharpoons CdS(s) + 2H^+(aq)$$

Dissolve copper sulphide by treating with dilute HNO_3 and evaporating to near dryness. Extract with water and neutralise with aqueous ammonia and confirm copper(II) by using $K_4[Fe(CN)_6]$ reagent.

Use of KCN to separate Cu(II) and Cd(II)

Solution containing $[Cu(NH_3)_4]^{2+}$ and $[Cd(NH_3)_4]^{2+}$ is treated with an excess of KCN prior to saturation with H_2S. $Cu^{2+}$is reduced to Cu^+ and a very stable complex $[Cu(CN)_3]^{2-}$ is produced ($K_f = 2.0 \times 10^{27}$).

$$2[Cu(NH_3)_4]^{2+}(aq) + 8CN^-(aq) \rightleftharpoons 2[Cu(CN)_3]^{2-}(aq) + (CN)_2(g) + 8NH_3(aq)$$

Consequently, concentration of Cu(I) ions in equilibrium with the complex is very low and K_{sp} of Cu_2S is not exceeded when the solution is saturated with H_2S.

Cadmium(II) ions form tetracyanocadmate(II) complex ions in the presence of cyanide ions. But the tetracyanocadmate(II) ions are much less stable ($K_f = 7.1 \times 10^{18}$)than the tricyanocuprate(I) ions, and they react with sulphide ions to form a yellow precipitate of cadmium sulphide:

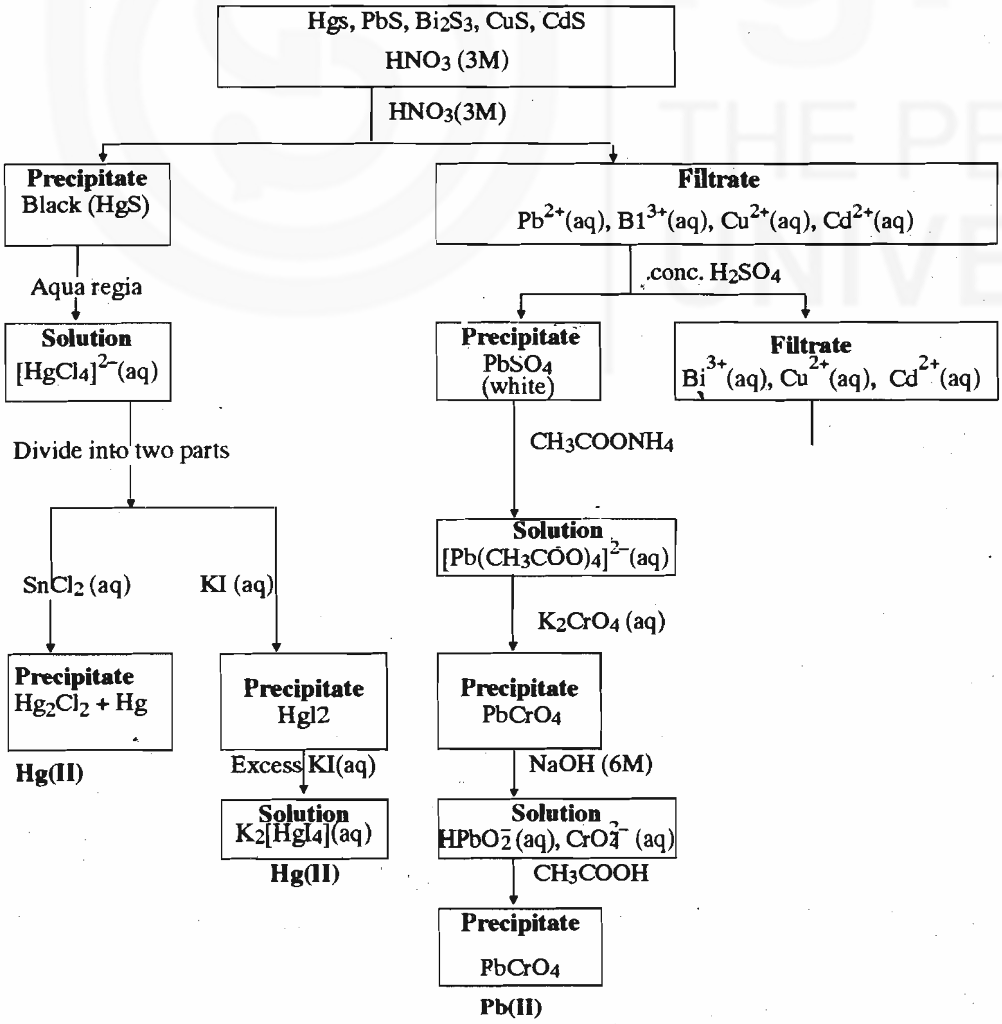
Potassium cyanide is a deadly poison. You may not have access to this chemical for performing the separation of copper and cadmium.

$$[Cd(NH_3)_4]^{2-}(aq) + 4CN^-(aq) \rightleftharpoons [Cd(CN)_4]^{2-}(aq) + 4NH_3(aq)$$

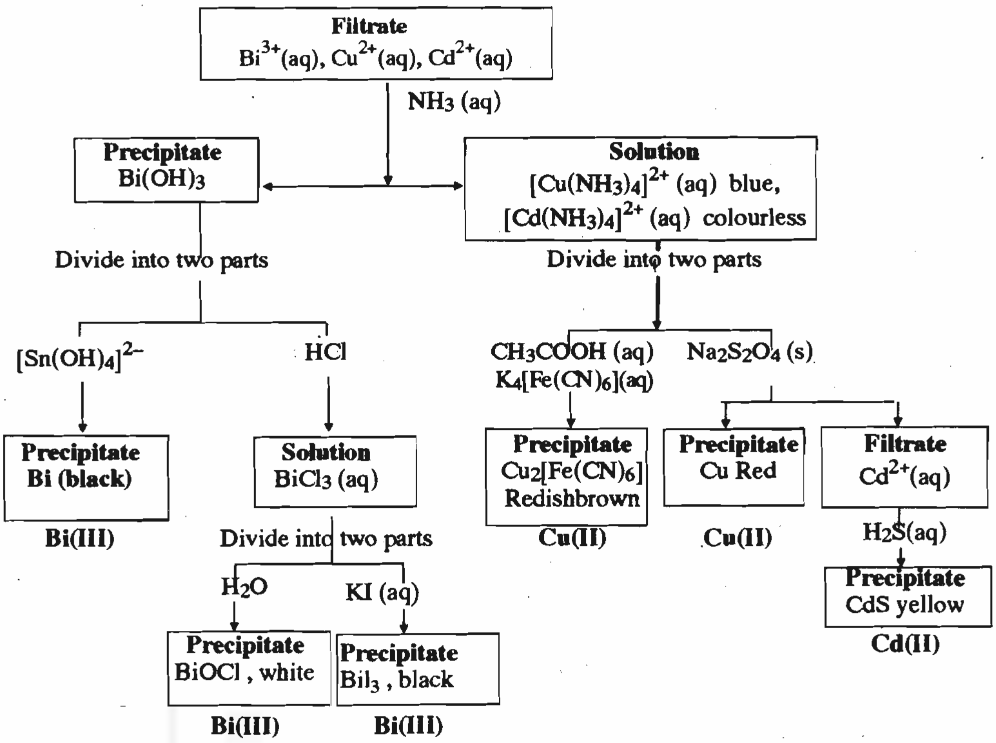
$$[Cd(CN)_4]^{2-}(aq) + S^{2-}(aq) \rightarrow CdS(s) + 4CN^-(aq)$$

The separation and identification of the cations of Group IIA is summarised in Flow Chart 6.4.

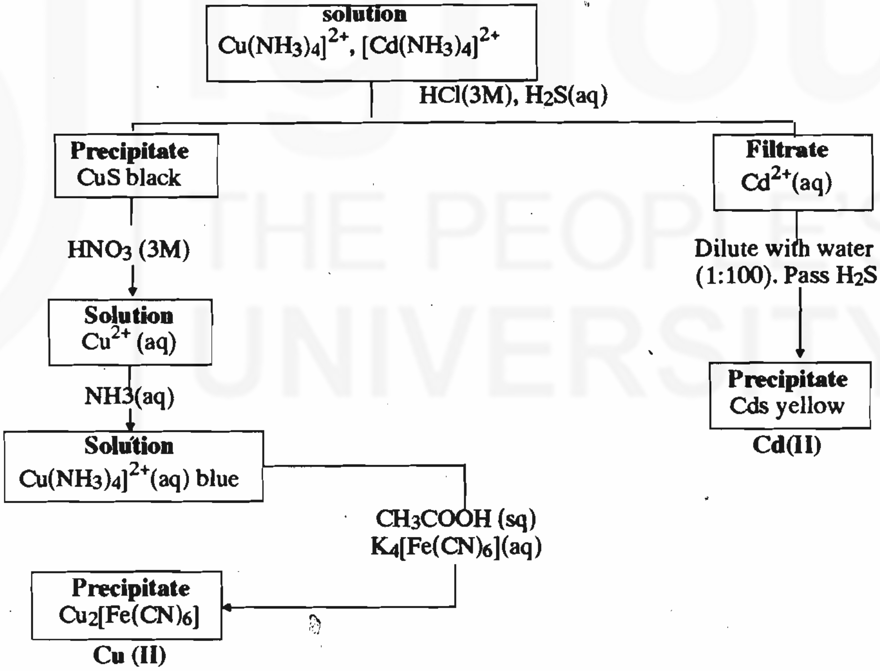
Flow Chart 6.4 : Separation and Identification of Group IIA Cations



Flow Chart 6.4 continued



Alternate Procedure for Separation of Cu(II) and Cd(II)



Identification of Arsenic(V)

Arsenate ion behaves very much like phosphate ion in its reactions. For example, when a solution of ammonium molybdate and nitric acid are added to a solution of arsenate ions, a yellow precipitate is formed:

$$AsO_4^{3-}(aq) + 12MoO_4^{2-}(aq) + 3NH_4^{+}(aq) + 24H^{+}(aq) \rightarrow (NH_4)_3[As(Mo_3O_{10})_4](s) + 12H_2O(l)$$

When magnesia mixture is added in the presence of ammonia, white insoluble magnesium ammonium arsenate precipitates :

$$AsO_4^{3-}(aq) + NH_4^{+}(aq) + Mg^{2+}(aq) + 6H_2O(l) \rightarrow MgNH_4AsO_4.6H_2O(s)$$

Further confirmation of arsenic(V.) involves dissolution of the precipitate in acetic acid and addition of $AgNO_3$ solution in the presence of ammonia(aq) when red-brown Ag_3AsO_4 precipitates:

$$MgNH_4AsO_4.6H_2O(s) + 2CH_3COOH(aq) \rightarrow$$
$$Mg^{2+}(aq) + NH_4^+(aq) + H_2AsO_4^-(aq) + 2CH_3COO^-(aq) + 6H_2O(l)$$

$$H_2AsO_4^-(aq) + 3Ag^+(aq) + 2NH_3(aq) \rightarrow Ag_3AsO_4(s) + 2NH_4^+(aq)$$

Identification of Tin(IV) and Atimony(III)

Sn(IV) and Sb(III) ions react with oxalic acid to form soluble complex compounds:

$$[SnCl_6]^{2-}(aq) + 3H_2C_2O_4(s) \rightarrow [Sn(C_2O_4)_3]^{2-}(aq) + 6Cl^-(aq) + 6H^+(aq)$$

$$[SbCl_4]^-(aq) + 3H_2C_2O_4(s) \rightarrow [Sb(C_2O_4)_3]^{3-}(aq) + 6H^+(aq) + 4Cl^-(aq)$$

For confirmation of tin(IV) in presence of antimony, add a piece of iron to the solution and heat on a water bath for 5 minutes. This reduces Sb(III) to Sb° and Sn(IV) to Sn(II). Filter the black deposit of antimony and add a few drops of $HgCl_2$ solution and wait. A white precipitate of Hg_2Cl_2 separates which turns gray on standing. If elemental iron is not available, a piece of aluminium wire may be substituted in the test.

$$2[SbCl_4]^-(aq) + 3Fe(s) \rightarrow 2Sb^\circ(s) + 3Fe^{2+}(aq) + 8Cl^-(aq)$$

$$[SnCl_6]^{2-}(aq) + Fe(s) \rightarrow [SnCl_4]^{2-}(aq) + Fe^{2+}(aq) + 2Cl^-(aq)$$

$$[SnCl_4]^{2-}(aq) + 2HgCl_2(aq) \rightarrow [SnCl_6]^{2-}(aq) + Hg_2Cl_2(s)$$

$$[SnCl_4]^{2-}(aq) + Hg_2Cl_2(s) \rightarrow [SnCl_6]^{2-}(aq) + 2Hg^\circ(l)$$

H_2S interferes with the test and must be boiled off before performing this test. High concentration of HCl should be avoided as it leads to the formation of stable $[HgCl_4]^{2-}$, which reduces the concentration of Hg^{2+} ions in solution. The separation and identification of the cations of Group IIB is summarised in Flow Chart 6. 5.

6.7 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP III

After the separation of cations of Group II, the filtrate from Group II is heated in a china dish to boil off H_2S gas. 5-6 drops of conc. HNO_3 are added and the solution again heated so as to oxidise iron(II) to iron(III), and H_2S, if any, to free sulphur:

$$3Fe^{2+}(aq) + 4H^+(aq) + NO_3^- \rightarrow 3Fe^{3+}(aq) + NO(g) + 2H_2O(l)$$

$$3H_2S(aq) + 2H^+(aq) + 2NO_3^-(aq) \rightarrow 3S(s) + 2NO(g) + 4H_2O(l)$$

The solution is buffered with $NH_4Cl - NH_4OH$ solution. The concentration of OH^- ion is controlled by adding NH_4^+ ions to the solution as a result of which only the hydroxides of Fe(III), Cr(III) and Al(III) are precipitated. The only remaining cation in the scheme that forms a precipitable hydroxide is Mg^{2+} ion. However, this hydroxide is much more soluble and would require a higher concentration of hydroxide ions than is available in the presence of NH_4^+ ions.

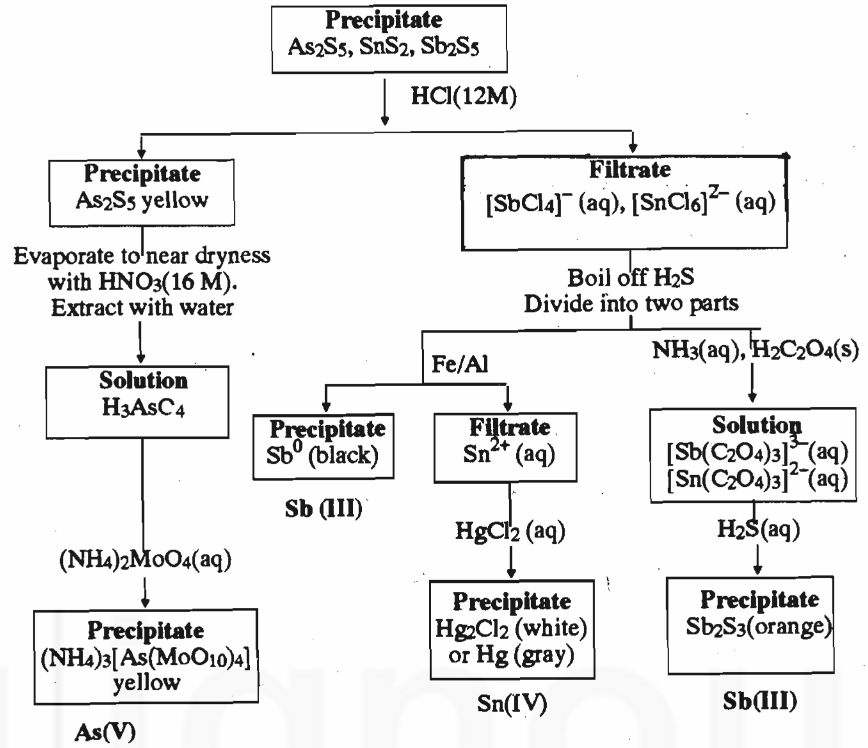
$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$$

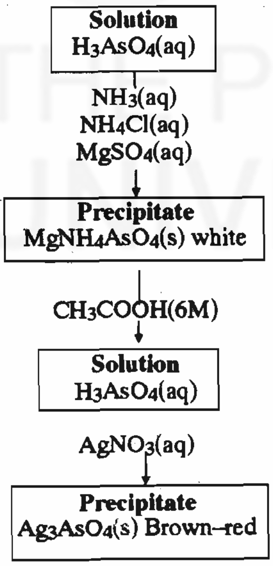
$$Al^{3+}(aq) + 3OH^{-}(aq) \rightarrow Al(OH)_3(s)$$

$$Cr^{3+}(aq) + 3OH^{-}(aq) \rightarrow Cr(OH)_3(s)$$

Flow Chart 6.5: Separation and Identification of Group IIB Cations



Identification of Arsenic(V)



Separation and Identification of the Cations of Analytical Group III

Aluminium and chromium hydroxides are amphoteric and readily dissolve in alkaline solution above pH 10.0 with the formation of $[Al(OH)_4(H_2O)_2]^{-}$(aq) (colourless) and $[Cr(OH)_4(H_2O)_2]^{-}$(aq) (green) complex species. Iron(III) hydroxide, however, does not dissolve in presence of excess alkali. Further the complex tetrahydroxochromate ion is easily oxidised to yellow chromate ion, CrO_4^{2-}(aq) by heating with H_2O_2, which is a strong oxidising agent in alkaline solution.

$$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons [Al(OH)_4(H_2O)_2]^-(aq)$$

$$Cr(OH)_3(s) + OH^-(aq) \rightleftharpoons [Cr(OH)_4(H_2O)_2]^-(aq)$$

$$2[Cr(OH)_4(H_2O)_2]^-(aq) + 2OH^-(aq) + 3H_2O_2(aq) \rightleftharpoons 2CrO_4^{2-}(aq) + 12H_2O(l)$$

Hence, separation of iron(III) from Al(III) and Cr(III) can be easily achieved.

Identification of Iron(III)

The brown coloured precipitate of $Fe(OH)_3$ is dissolved in dil. HNO_3 to give a light yellow solution containing $Fe^{3+}(aq)$. The presence of Fe^{3+} is confirmed by the formation of characteristic colour of Prussian blue, $KFe[Fe(CN)_6]$ or the blood red thiocyanatoferrate(III) iron, $[Fe(NCS)(H_2O)_5]^{2+}$:

$$Fe^{3+}(aq) + K^+(aq) + [Fe(CN)_6]^{4-}(aq) \rightarrow KFe[Fe(CN)_6](s)$$

$$[Fe(H_2O)_6]^{3+}(aq) + NCS^-(aq) \rightleftharpoons [Fe(NCS)(H_2O)_5]^{2+}(aq) + H_2O(l)$$

A large number of complexes exist in solution depending on the concentration of thiocyanate. However, these complexes dissociate on dilution with water. Therefore, a high concentration of thiocyanate should be maintained while performing this test.

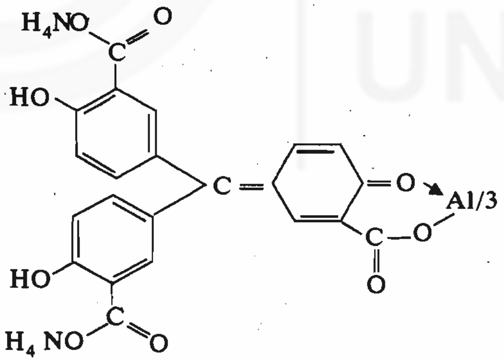
Identification of Aluminium(III)

The solution containing diaquotetrahydroxoaluminate(III), $[Al(OH)_4(H_2O)_2]^-$, on careful acidification or boiling with NH_4Cl reprecipitates aluminium hydroxide:

$$[Al(OH)_4(H_2O)_2]^-(aq) + H^+(aq) \rightarrow Al(OH)_3(s) + 3H_2O(l)$$

$$[Al(OH)_4(H_2O)_2]^-(aq) + NH_4^+(aq) \rightarrow Al(OH)_3(s) + NH_3(g) + 3H_2O(l)$$

The presence of aluminium ions in the solution can be further confirmed by addition of aluminon, the ammonium salt of aurinetricarboxylic acid, which gives an insoluble red coloured lake. Blue litmus solution can also be used in place of aluminon reagent.



In case of blue litmus solution, a blue floating lake is observed in the solution when ammonia is continuously added down the side of the test tube containing an acidified solution of aluminium(III). The dye gets adsorbed on the precipitate of gelatinous aluminium hydroxide.

$$Al^{3+}(aq) + 3NH_3(aq) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3NH_4^+(aq)$$

Identification of Chromium(III)

If the solution after oxidation is coloured yellow, it shows the presence of chromate ions, CrO_4^{2-}. This solution on acidification turns orange due to the existence of a pH dependent equilibrium :

$$2CrO_4^{2-}(aq) \underset{OH^-(aq)}{\overset{H^+(aq)}{\rightleftharpoons}} Cr_2O_7^{2-}(aq)$$

The presence of chromium is confirmed by the acidification of solution containing CrO_4^{2-} in the presence of H_2O_2, when a blue colour appears, which rapidly fades producing free oxygen. The colour can be stabilised if amyl alcohol or ether is added before adding H_2O_2:

$$Cr_2O_7^{2-}(aq) + 4H_2O_2(aq) + 2H^+(aq) \rightarrow 2CrO_5(aq) + 5H_2O(l)$$

$$4CrO_5(aq) + 12H^+(aq) \rightarrow 4Cr^{3+}(aq) + 7O_2(g) + 6H_2O(l)$$

Addition of either Pb^{2+} or Ba^{2+} to a solution of CrO_4^{2-} ions made acidic with acetic acid produces yellow precipitate of $PbCrO_4$ or $BaCrO_4$:

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightleftharpoons BaCrO_4(s)$$

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightleftharpoons PbCrO_4(s)$$

The yellow precipitate, however, dissolves in the presence of strong acid.

$$2BaCrO_4(s) + 2H^+(aq) \rightleftharpoons 2Ba^{2+}(aq) + Cr_2O_7^{2-}(aq) + H_2O(l)$$

The separation and identification of the cations of Group III is summarised in Flow Chart 6.6.

6.8 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP IV

The filtrate after separation of Group III cations contains ammine complexes of cobalt(II), nickel(II) and zinc(II) and $Mn(OH)_2$, which does not precipitate because the $[OH^-]$ is controlled by the NH_4^+ ion added as NH_4Cl.

$$Co^{2+}(aq) \xrightarrow{NH_3(aq)} Co(OH)_2(s) \xrightarrow{NH_3(excess)} [Co(NH_3)_6]^{2+} \text{ tan}$$

$$Ni^{2+}(aq) \xrightarrow{NH_3(aq)} Ni(OH)_2(s) \xrightarrow{NH_3(excess)} [Ni(NH_3)_6]^{2+} \text{ deep blue}$$

$$Zn^{2+}(aq) \xrightarrow{NH_3(aq)} Zn(OH)_2(s) \xrightarrow{NH_3(excess)} [Zn(NH_3)_4]^{2+} \text{ colourless}$$

The sulphides of this group have larger K_{sp} values than the sulphides of Group II and, therefore, would require higher concentration of S^{2-} ions for precipitation.

H_2S produces S^{2-} according to the reaction $H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$. In the preceding unit, you have studied that the S^{2-} ion concentration can be controlled by controlling the H^+ ion concentration. If the $[H^+]$ decreases, then the $[S^{2-}]$ will increase as a new equilibrium will be established through an increased forward reaction. To produce the desired $[S^{2-}]$, a ammonium hydroxide controlled reaction is used to reduce $[H^+]$ by means of the strong forward reaction $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$. By decreasing the H^+ ion concentration still further, the S^{2-} concentration is increased as the reaction $H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$ shifts still further to the right. The cations of this group are, therefore, precipitated from NH_4Cl–NH_4OH buffered solution as sulphides by passing H_2S:

$$[Co(NH_3)_6]^{2+}(aq) + S^{2-}(aq) \rightarrow CoS(s) + 6NH_3(aq)$$

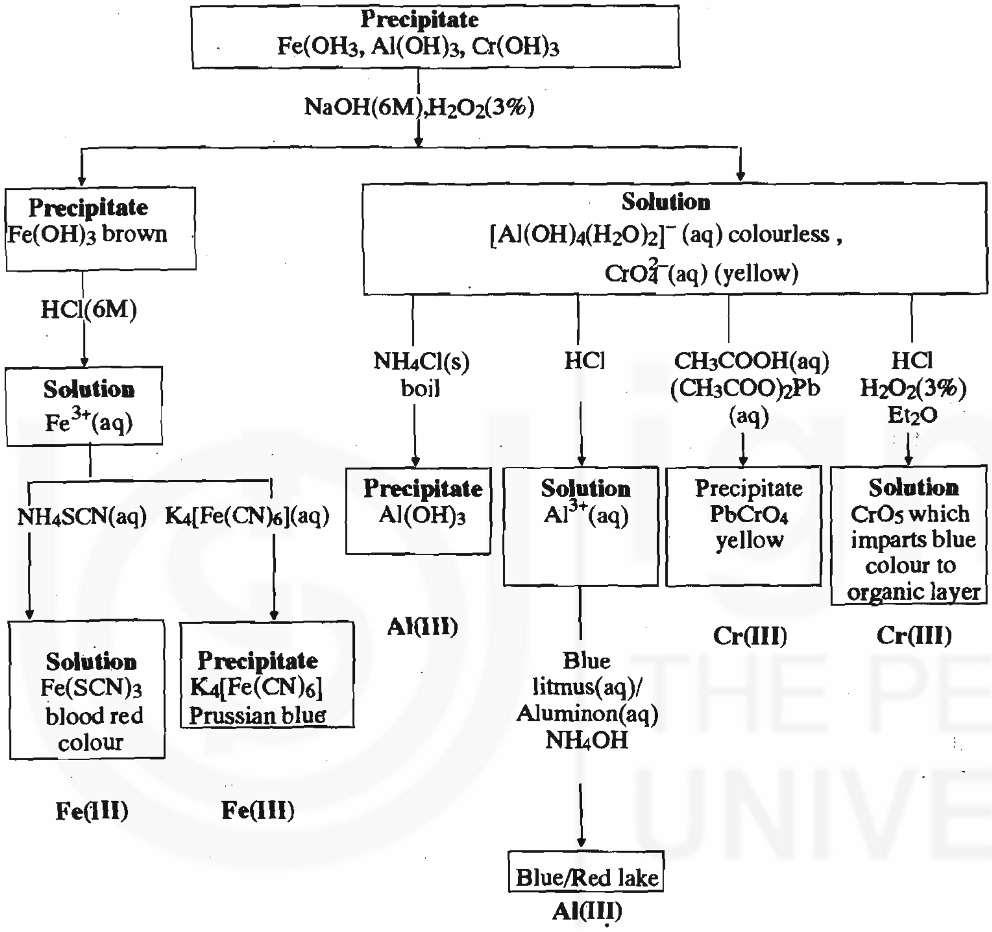
$$[Ni(NH_3)_6]^{2+}(aq) + S^{2-}(aq) \rightarrow NiS(s) + 6NH_3(aq)$$

$$Mn^{2+}(aq) + S^{2-}(aq) \rightarrow MnS(s)$$

$$[Zn(NH_3)_4]^{2+}(aq) + S^{2-}(aq) \rightarrow ZnS(s) + 4NH_3(aq)$$

Two forms of cobalt sulphide exist, α-CoS, which is readily soluble in HCl(6 M). However, the α-CoS on standing converts spontaneously to ß-CoS, which is slightly soluble in dilute HCl. Freshly precipitated NiS has a tendency to convert to colloidal form. Therefore, before filtration, it is desirable to add $NH_4Cl(s)$ and warm the solution in a water bath which not only flocculates the precipitate but also converts α-CoS to ß-CoS.

Flow Chart 6.6 : Separation and Identification of Cations of Gropp III



Separation and Identification of the Cations of Analytical Group IV

The cations of this group can be separated into nickel-cobalt and zinc-manganese subgroups. Zinc and manganese sulphides readily dissolve in dilute HCl, while cobalt and nickel sulphides are sparingly soluble. Therefore, the precipitate of the Group IV cations is treated with dil. HCl to separate them into two sub-groups. ZnS and MnS pass into solution, whereas CoS and NiS remain as residue which is separated by filtration.

$$MnS(s) + 2H^+(aq) \rightarrow Mn^{2+}(aq) + H_2S(g)$$

$$ZnS(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2S(g)$$

The solution now contains Mn(II) and Zn(II). The solution is boiled to expel H_2S and Zn(II) is separated from Mn(II) by taking advantage of the amphoteric character of zinc hydroxide, which dissolves in presence of excess alkali. The solution, therefore, when boiled with NaOH converts zinc(II) to soluble tetrahydroxozincate(II), $[Zn(OH)_4]^{2-}$, leaving a black-brown $MnO_2 . xH_2O$. Oxidation of black MnO_2 by H_2O_2 in nitric acid brings Mn(II) into solution.

$$Zn^{2+}(aq) + 4OH^-(aq) \rightleftharpoons [Zn(OH)_4]^{2-}(aq)$$

$$Mn^{2+}(aq) + 2OH^-(aq) \rightarrow Mn(OH)_2(s)$$

$$Mn(OH)_2 + H_2O_2(aq) \rightarrow MnO_2(s) + 2H_2O(l)$$

$$MnO_2(s) + H_2O_2(aq) + 2H^+(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + O_2(g)$$

The residue of CoS and NiS is then dissolved in aqua regia.

$$CoS(s) + HNO_3(aq) + 3HCl(aq) \rightarrow Co^{2+}(aq) + S(s) + NOCl(g) + 2Cl^-(aq) + 2H_2O(l)$$

$$NiS(s) + HNO_3(aq) + 3HCl(aq) \rightarrow Ni^{2+}(aq) + S(s) + NOCl(g) + 2Cl^-(aq) + 2H_2O(l)$$

On longer heating the mixture becomes clear because sulphur gets oxidised to sulphate ions:

$$S(s) + 4NO_3^-(aq) \rightarrow SO_4^{2-}(aq) + 4NO_2(g)$$

Identification of Zinc(II)

The presence of zinc(II) can be confirmed either by reprecipitation of zinc sulphide or by production of a gray white precipitate of $K_2Zn_3[Fe(CN)_6]_2$ in acidic solution. Most other hexacyanoferrates are soluble in acidic solution, whereas the gray-white precipitate dissolves in basic solution.

$$Zn^{2+}(aq) + S^{2-}(aq) \rightleftharpoons ZnS(s)$$

$$3Zn^{2+}(aq) + 2K^+(aq) + 2[Fe(CN)_6]^{4-}(aq) \rightarrow K_2Zn_3[Fe(CN)_6]_2(s)$$

$$K_2Zn_3[Fe(CN)_6]_2(s) + 12OH^-(aq) \rightarrow 2K^+(aq) + 3[Zn(OH)_4]^{2-}(aq) + 2[Fe(CN)_6]^{4-}(aq)$$

Identification of Manganese(II)

When the brown precipitate of manganese(IV) oxide is dissolved in H_2O_2 containing nitric acid and the oxidation effected by a powerful oxidant like sodium bismuthate(V) or lead(IV) oxide, conversion to purple permanganate ion, MnO_4^-, takes place. This is an excellent confirmatory test for the detection of manganese(II).

$$MnO_2(s) + H_2O_2(aq) + 2H^+(aq) \rightarrow Mn^{2+}(aq) + O_2(g) + 2H_2O(l)$$

$$2Mn^{2+}(aq) + 14H^+(aq) + 5NaBiO_3(s) \rightarrow 2MnO_4^-(aq) + 5Bi^{3+}(aq) + 7H_2O(l) + 5Na^+(aq)$$

Identification of Cobalt(II)

Cobalt is identified by the golden yellow colour of potassium hexanitritocobaltate(III) or by the blue colour of thiocyanato complex, $[Co(NCS)_4]^{2-}$ or by the red colour of 1-nitroso-2-naphtholate complex.

Add potassium nitrite to the solution and acidify with acetic acid when hexanitritocobaltate(II), $[Co(NO_2)_6]^{4-}$, forms which gets oxidised to hexanitritocobaltate(III) ion, $[Co(NO_2)_6]^{3-}$:

$$Co^{2+}(aq) + 6NO_2^-(aq) \rightarrow [Co(NO_2)_6]^{4-}(aq)$$

$$[Co(NO_2)_6]^{4-}(aq) + NO_2^-(aq) + 2H^+(aq) \rightarrow [Co(NO_2)_6]^{3-}(s) + NO(g) + H_2O(aq)$$

This in turn reacts with potassium ions in solution to precipitate golden yellow potassium hexanitritocobaltate(III).

$$3K^+(aq) + [Co(NO_2)_6]^{3-}(aq) \rightarrow K_3[Co(NO_2)_6](s)$$

The overall reaction can be expressed as follows:

$$Co^{2+}(aq) + 7KNO_2(s) + 2H^+(aq) \rightarrow K_3[Co(NO_2)_6](s) + NO(g) + 4K^+(aq) + H_2O(l)$$

Other tests may also be performed to confirm the presence of cobalt in the solution.

Add amyl alcohol or ether and solid ammonium thiocyanate, followed by concentrated hydrochloric acid. Deep blue colour in alcohol or ether layer confirms cobalt(II).

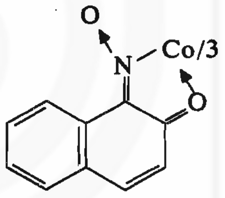
$$Co^{2+}(aq) + 4SCN^-(aq) \rightleftharpoons \underset{\text{Tetrathiocyanatocobaltate(II)}}{[Co(SCN)_4]^{2-}}$$

$$2H^+(aq) + [Co(SCN)_4]^{2-} \rightleftharpoons \underset{\text{Deep blue colour in amyl alcohol or ether}}{H_2[Co(SCN)_4]}$$

Since Fe(III) forms a blood red coloured complex, $[Fe(NCS)(H_2O)_5]^{2+}$, which would interfere with the test for cobalt. Addition of sodium fluoride prevents interference of Fe(III) due to formation of stable $[FeF_6]^{3-}$ complex ion.

$$[Fe(H_2O)_6]^{3+}(aq) + 6F^-(aq) \rightarrow [FeF_6]^{3-}(aq) + 6H_2O(l)$$

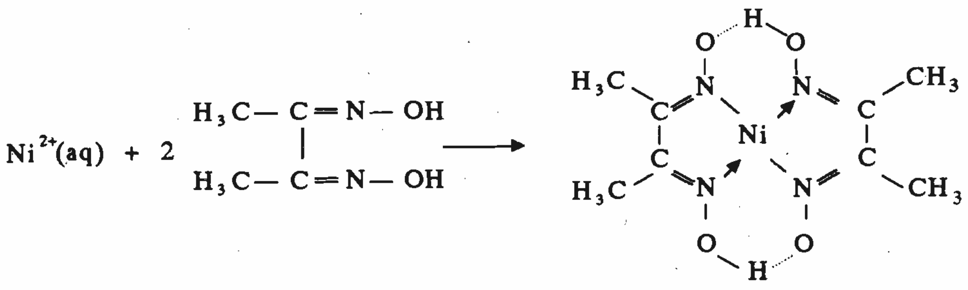
Add 1-notroso-2-naphthol reagent. An orange red precipitate forms, which is extractable into chloroform. A number of other metal ions, like nickel(II), copper(II), iron(II) etc. also form insoluble precipitates with this reagent. Cobalt forms a complex, which is inert and is unaffected even in the presence of concentrated hydrochloric acid, other complexes dissociate and go back into aqueous phase.



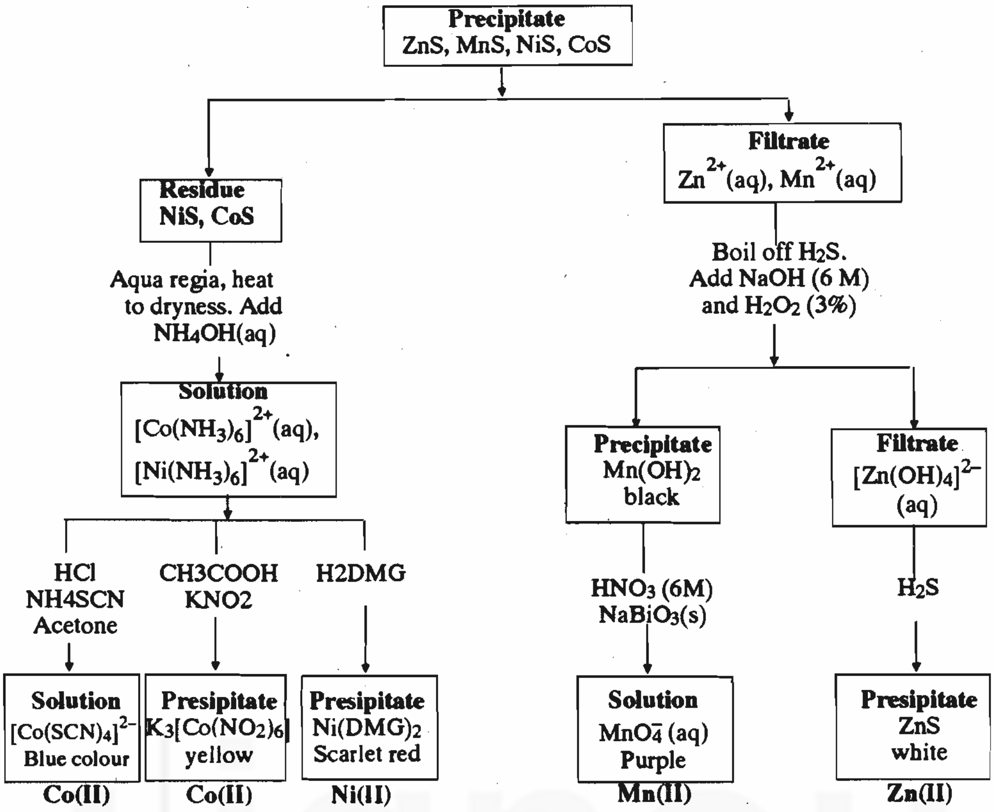
Identification of Nickel(II)

The presence of nickel in the solution is confirmed by addition of dimethyl glyoxime reagent when a scarlet red complex is formed. Cobalt(II) also complexes with the reagent but the complex does not precipitate and so cobalt does not interfere in the detection of nickel.

The separation and identification of the cations of Group IV is summarised in Flow Chart 6.7.



Flow Chart 6.7 : Separation and Identification of Cations of Group IV



6.9 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP V

The solution after separation of Group IV cations contains Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+} and K^+, besides a very high concentration of NH_4^+ salts. The solution is acidified with HCl and boiled to expel H_2S. Ammonium salts can be decomposed either by strong heating or heating with concentrated HNO_3 at elevated temperatures.

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$

$$NH_4NO_3(s) \rightarrow NH_3(g) + HNO_3(g)$$

$$NH_3(g) + HNO_3(g) \rightarrow N_2O(g) + 2H_2O(l)$$

The cations of this group are precipitated as carbonates by addition of $(NH_4)_2CO_3$ from a $NH_4Cl - NH_4OH$ buffered solution.

$$Ba^{2+}(aq) + CO_3^{2-}(aq) \rightarrow BaCO_3(s)$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$

$$Sr^{2+}(aq) + CO_3^{2-}(aq) \rightarrow SrCO_3(s)$$

Separation and Identification of the Cations of Analytical Group V

The separation of the cations of this group is achieved by taking advantage of the analytically useful difference in the solubilities of chromates. Calcium chromate is soluble. Barium chromate can be precipitated. However, if the concentration of CrO_4^{2-} ions is high, $SrCrO_4$ can coprecipitate. The presence of acetic acid decreases the concentration of CrO_4^{2-} ions and allows only $BaCrO_4$ to precipitate leaving Sr(II) and Ca(II) in solution. Any possible coprecipitation of $SrCrO_4$ is further prevented by precipitation from hot solution.

The carbonates of this group are dissolved in acetic acid and barium chromate is precipitated by addition of K_2CrO_4.

$$BaCO_3(s) + 2H^+(aq) \rightarrow Ba^{2+}(aq) + H_2O(l) + CO_2(g)$$

$$CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$$

$$SrCO_3(s) + 2H^+(aq) \rightarrow Sr^{2+}(aq) + H_2O(l) + CO_2(g)$$

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow BaCrO_4(s)$$

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$$

Even though the K_{sp} values of $SrSO_4$ and $CaSO_4$ are also close to each other, only $SrSO_4$ precipitates when $(NH_4)_2SO_4$ is added to the solution. Possibly Ca(II) forms soluble sulphato complex, $[Ca(SO_4)_2]^{2-}$. So using a moderate concentration of SO_4^{2-} ions, $SrSO_4$ can be precipitated leaving Ca^{2+} in solution:

$$Sr^{2+}(aq) + SO_4^{2-}(aq) \rightarrow SrSO_4(s)$$

Identification of Barium(II)

The presence of barium in solution is confirmed by the precipitation of yellow $BaCrO_4$ on addition of potassium chromate. Strontium chromate may also precipitate if the concentration of CrO_4^{2-} ions is high enough. The presence of acetic acid decreases the concentration of CrO_4^{2-} ions so that $SrCrO_4$ does not precipitate. The pH of the solution is maintained at 7.0 by addition of ammonium acetate.

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow BaCrO_4(s)$$

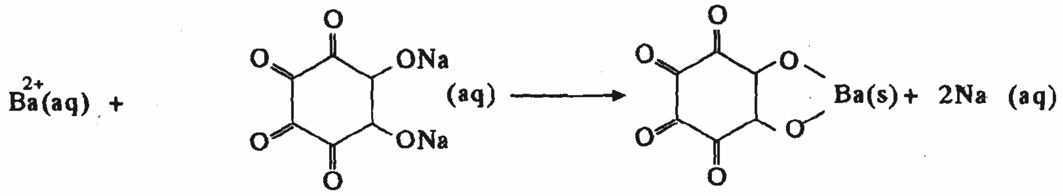
Further confirmation may be done by converting barium chromate to barium chloride by addition of hydrochloric acid and (i) performing the flame test or (ii) by precipitating white $BaSO_4$.

$$2BaCrO_4(s) + 2H^+(aq) \rightarrow 2Ba^{2+}(aq) + Cr_2O_7^{2-}(aq) + H_2O(l)$$

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

Barium imparts a grassy green colour to the non-luminous flame.

Detection of barium can also be done by spotting a drop of solution containing Ba^{2+} ions on a filter paper and by adding a drop of sodium rhodizonate solution. Appearance of a red-brown spot confirms the presence of barium. The colour remains unaffected even on addition of dilute HCl.



Identification of Strontium(II)

The presence of strontium(II) ions in solution is confirmed by the addition of saturated $(NH_4)_2SO_4$ solution, when white $SrSO_4$ precipitates. Though the K_{sp} values for $SrSO_4$ and $CaSO_4$ are very close to each other, $CaSO_4$ does not precipitate possibly due to the formation of calcate(II) ion,$[Ca(SO_4)_2]^{2-}$:

$$Sr^{2+}(aq) + SO_4^{2-}(aq) \rightarrow SrSO_4(s)$$

The precipitate of $SrSO_4$ is converted to $SrCO_3$ by transposition with sodium carbonate solution.

$$SrSO_4(s) + CO_3^{2-}(aq) + 2Na^+(aq) \rightleftharpoons SrCO_3(s) + 2Na^+(aq) + SO_4^{2-}(aq)$$

Finally perform flame test after converting $SrCO_3$ to $SrCl_2$ by addition of hydrochloric acid.

$$SrCO_3(s) + 2H^+(aq) + 2Cl^- \rightarrow Sr^{2+}(aq) + 2Cl^-(aq) + CO_2(g) + H_2O(l)$$

A red or scarlet colour is imparted to the flame. The colour is visible through single cobalt blue glass, but is not visible while seen through multilayers of blue glasses (distinction from K^+).

Further confirmation can be done using neutral solution and spotting on a filter paper and adding a drop of sodium rhodizonate when a red-brown spot is obtained. Strontium rhodizonate is, however, soluble in dilute HCl (distinction from barium) and the colour disappears on addition of dil. HCl.

Identification of Calcium(II)

The presence of calcium in solution is detected by precipitating calcium oxalate from neutral or slightly alkaline solution. The precipitate is insoluble in acetic acid medium. It, however, precipitates slowly and, therefore, the concentration of the acid should be suitably adjusted by addition of ammonium hydroxide to enhance precipitation.

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow CaC_2O_4(s)$$

Perform flame test after dissolving CaC_2O_4 in hydrochloric acid. A brick-red colour is imparted to the flame.

$$CaC_2O_4(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq) + 2H^+(aq) + C_2O_4^{2-}(aq)$$

Confirmation of Ba^{2+}, Sr^{2+} and Ca^{2+} by Flame Tests

Chlorides of barium, strontium, calcium, sodium, potassium and some other metals, when fed into a non-luminous Bunsen burner flame, impart a characteristic colour to the flame. The colour of the flame is then used to identify the metal chloride fed into the flame. This type of test is known as the flame test.

When the chlorides of above mentioned metals are fed into the flame, they are volatilised and dissociated into metal and the chlorine atoms. The burner flame is hot enough to promote electrons in metal atoms to higher energy levels. As these excited metal atoms move out of the hot region of the flame, electrons drop back to their ground state energy levels and energy is liberated. When the energy liberated is emitted as visible light, the atoms impart characteristic colours to the flame because the differences between energy levels are very specific and correspond to light of specific wavelengths in the visible region. The electronic transitions which take place during a flame test can be represented as shown in Fig. 6.1.

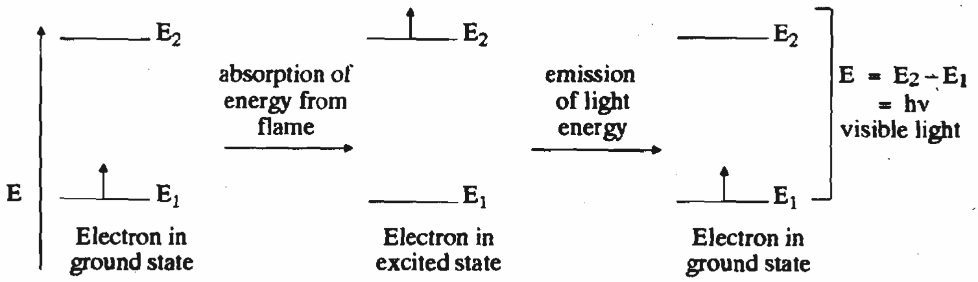


Fig. 6.1 : Electronic Transitions in a Flame Test

Flame tests are performed with a piece of platinum wire sealed into the end of a glass tubing or stuck into a small cork. Flame tests are very sensitive, therefore, the wire must be perfectly clean before a flame test is performed. The end of the wire is bent into a small loop so that, when it is dipped into a solution, a film of liquid covers the loop. The burner flame is adjusted so that it is as hot as possible and there is a well defined blue cone with very little colour in the outer part of the flame. The wire loop is dipped in dilute HCl (6 M), brought slowly up to the outer edge of the blue cone, and held there until the loop is red hot. The hot loop is dipped in dilute HCl again and the operation is repeated until the wire imparts no colour to the flame (Fig. 6.2).

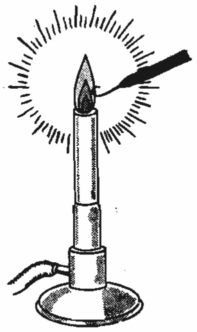


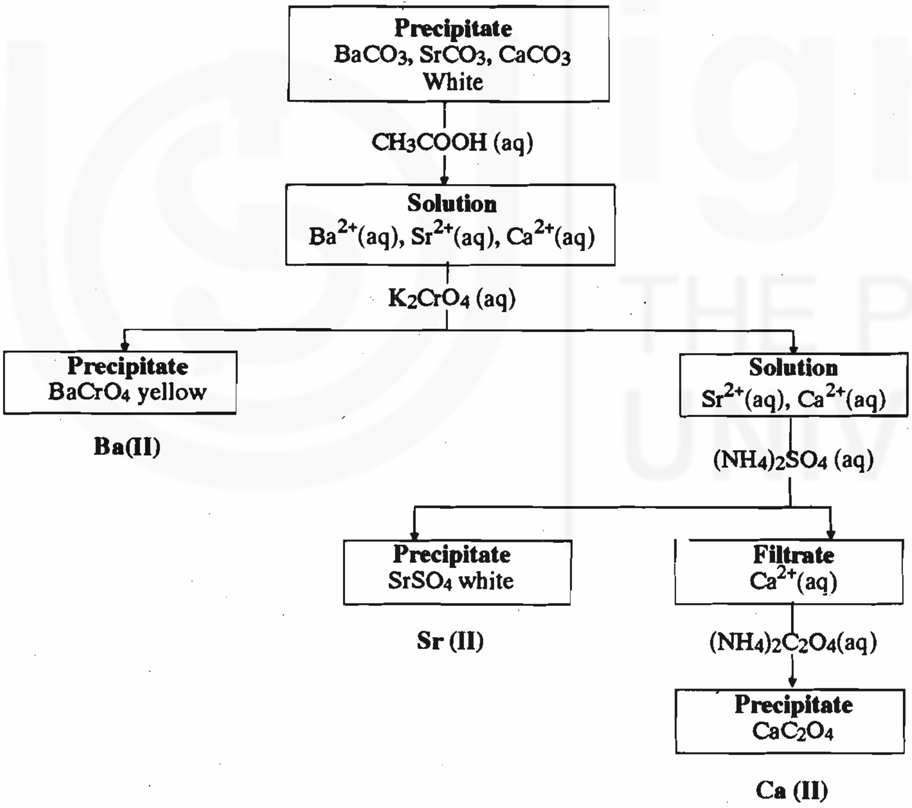
Fig. 6.2 : Performing a Flame Test

The clean wire is then dipped into the solution to be flame-tested and brought up to the outer edge of the blue cone. The cations of Group V and Group zero impart the following colours to flame:

Ba^{2+}	apple-green
Sr^{2+}	crimson-red
Ca^{2+}	brick-red
Na^{2+}	intense yellow
K^{+}	violet

The separation and identification of the cations of Group V is summarised in Flow Chart 6.8.

Flow Chart 6.8 : Separation and Identification of Cations of Group V



6.10 ANALYSIS OF THE CATION OF ANALYTICAL GROUP VI

Magnesium(II) is the only cation left in solution along with potassium and NH_4^+. It is convenient to analyse NH_4^+ and K^+ ions prior to the analysis of Group I cations. Magnesium precipitates from ammonical solution by addition of diammonium or disodium hydrogen phosphate as white magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$.

$$Mg^{2+}(aq) + NH_4^+(aq) + PO_4^{3-}(aq) + 6H_2O(l) \rightarrow MgNH_4PO_4.6H_2O(s)$$

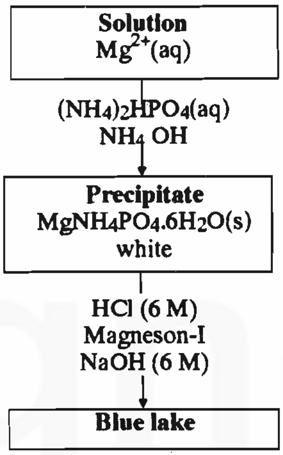
The precipitate dissolves readily in dilute HCl

$$MgNH_4PO_4.6H_2O(s) + 2H^+(aq) \rightleftharpoons Mg^{2+}(aq) + NH_4^+(aq) + H_2PO_4^-(aq) + 6H_2O(l)$$

Identification of Cation of Group VI

Treat the solution containing magnesium ions with magneson-I reagent (p-nitrobenzeneazoresorcinol) and sodium hydroxide. A blue solid lake containing the adsorbed dye on the surface of $Mg(OH)_2$ precipitate forms (the reagent is orange-red in solution). Identification of magnesium(II) is summarised in Flow Chart 6.9.

Flow Chart 6.9 : Identification of Mg(II)



6.11 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP ZERO

The cations, which are not precipitated as chlorides, hydroxides, sulphides, carbonates or phosphates comprise the members of this group, sometimes called the 'soluble group'. Sometimes the cations of this group are also referred to as 'Zero Group' cations, since it is advisable to identify these cations prior to the analysis of Group I cations. The members of this group include sodium, potassium, rubidium, caesium and ammonium etc. Here we will discuss the identification of NH_4^+ and K^+ ions only.

Solubility behaviour of NH_4^+ and K^+ salts is almost similar because of similar ionic radii (K^+ = 133pm, NH_4^+ = 143pm). For this reason removal of NH_4^+ ion before detection of K^+ ion by precipitation is essential to avoid any possible interference.

Separation of these cations is not necessary since independent tests are available for their identification. It is, therefore, advisable to perform tests directly with the original sample or its aqueous extract rather than with the solution obtained after the analysis of Group VI cations.

Identification of Ammonium ion (NH_4^+)

Heating ammonium salts with a stronger base (OH^- ion) liberates ammonia which can be detected by the following tests:

i) its characteristic odour (do not sniff the vapour directly)

ii) dense white fumes with HCl

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$$

$$NH_3(aq) \rightleftharpoons NH_3(g)$$

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(g)$$

iii) the change in colour of the moist red litmus to blue when exposed to NH_3 vapour.

iv) its reaction with alkaline Nessler's reagent which turns brown.

$$4NH_3(g) + 2[HgI_4]^{2-}(aq) \xrightarrow{OH^-(aq)} Hg_2NI(s) + 7I^-(aq) + 3NH_4^+(aq)$$

v) formation of a yellow precipitate with sodium hexanitritocobaltate(III), $Na_3[Co(NO_2)_6]$:

$$2NH_4^+(aq) + Na_3[Co(NO_2)_6](aq) \rightarrow (NH_4)_2Na[Co(NO_2)_6](s) + 2Na^+(aq)$$

Diammonium sodium hexanitritocobalte(III)

In the following section, you will learn that potassium ions also give a yellow precipitate with $Na_3[Co(NO_2)_6]$.

Identification of Potassium (K^+)

Potassium is detected in aqueous solution by addition of sodium hexanitritocobaltate(III), $Na_3[Co(NO_2)_6]$, when yellow coloured dipotassium sodium hexanitritocobaltate(III), $K_2Na[Co(NO_2)_6]$, precipitates:

$$2K^+(aq) + 3Na^+(aq) + [Co(NO_2)_6]^{3-}(aq) \rightarrow K_2Na[Co(NO_2)_6](s) + 2Na^+(aq)$$

The presence of strong acid destroys the nitrite ion. Therefore, sodium nitrite(s) should invariably be added to the reagent solution before performing this test. Preferably use a freshly prepared reagent solution. Presence of oxidising agents and OH^- ions changes the composition of the reagent and renders it ineffective.

$$3NO_2^-(aq) + 2H^+(aq) \rightarrow 2NO(g) + NO_3^-(aq) + H_2O(l)$$

It is convenient to perform the flame test using the yellow precipitate since the precipitate concentrates K^+ ions. Potassium ions give a crimson-violet colour when seen through multilayers of blue cobalt glasses. No other ion interferes even if the test is performed with the mixture of salts.

Identification of Potassium(K^+) and Ammonium (NH_4^+) Ions When Present Together

The presence of NH_4^+ ions can be detected by the distinctive reaction resulting in the evolution of ammonia when heated with a strong base. [See test under identification of NH_4^+ ion.]

Since both the cations give yellow precipitates with $Na_3[Co(NO_2)_6]$, ammonium salts must be destroyed before testing for K^+ ion in the solution. A convenient method is to heat the ammonium salts with concentrated nitric acid (5-10 drops) to dryness, extracting the residue with water and testing for the absence of ammonium ions with alkaline Nessler's reagent.

$$NH_4^+(aq) + NO_3^-(aq) \xrightarrow{H^+(aq)} N_2O(g) + 2H_2O(g)$$

Once the absence of NH_4^+ ion is confirmed in solution, K^+ ions can be detected with $Na_3[Co(NO_2)_6]$. Alternatively, a flame test may be done using the mixture of salts. Further confirmation for K^+ ions may be obtained by addition of sodium tetraphenylboron reagent, $Na[B(C_6H_5)_4]$, when a white precipitate of potassium tetraphenylboron is formed:

$$K^+(aq) + Na[B(C_6H_5)_4] \rightarrow K[B(C_6H_5)_4](s) + Na^+(aq)$$

6.12 SUMMARY

In this unit you studied the scheme of qualitative analysis of the cations present in an inorganic mixture. You studied the separation of the cations into seven analytical groups by selective precipitation. Selective precipitation is performed by the addition of the group reagents in a sequential manner. You also learnt the confirmatory tests for identification of various cations. The procedure for analysis of the cations is given in Schemes 6.1 to 6.8 in the Appendix.

6.13 FURTHER READING

Vogel's Qualitative Inorganic Analysis, G. Svehla, Orient Longman, Sixth edition, 1987.