Mixture Separation

(Qualitative Analysis)

Aim

- To separate and identify some common cations present in an inorganic mixture of salts by performing various tests.

Theory

- Qualitative analysis is the systematic approach that involves precipitation reaction to remove cations sequentially from a mixture. The behavior of the cations toward a set of common test reagents differs from one cation to another and furnishes the basis for their separation.

Materials and Tools Required

1. Test tubes
2. Boiling tubes
3. Test tube holder
4. Test tube stand
5. Flame
6. Reagents
7. Centrifuge

Group I Cations
(Ag^{+}, Hg_2^{2+} and Pb^{2+})

silver mercurous lead

Reagent : dil. HCl

Cations form insoluble chlorides with hydrochloric acid. When diluted HCl is added to the solution, white precipitates of AgCl, Hg_2Cl_2 and $PbCl_2$ are formed. Other metallic cations remain in solution.

Group II Cations

IIA: (Hg^{2+}, Cd^{2+}, Cu^{2+}, $Bi^{3}+$)

mercuric cadmium cupric bismuth

IIB: (As^{3+}, Sb^{3+} and As^{5+})

stannus antimony arsenic

Reagent : dil. HCl + H_2S

The pH of the solution is adjusted to 0.5 and then H_2S is added. Since the concentration of sulfide ion (s^{2-}) is very low at low pH, only Gr.II sulfides having very low Ksp values will precipitate. Cations with larger Ksp values for Gr.IV sulfides remain in solution.

Group III Cations
(Al^{3+}, Fe^{3+}, Fe^{2+} and Cr^{3+})

Aluminum ferric ferrous chromic

Reagent : ($NH_4Cl + NH_4OH$) = Buffer solution

Since the solution is basic Al^{3+}, Fe^{3+} and Cr^{3+} form insoluble hydroxides and are also separated from the solution.

Group IV Cations
(Co^{2+}, Ni^{2+}, Zn^{2+} and Mn^{2+})

cobalt nickel zinc manganese

Reagent : ($NH_4Cl + NH_4OH$) + H_2S

After isolating the insoluble sulfides in acidic medium, the solution is made basic and the metallic sulfides having larger Ksp values such as ZnS, NiS, CoS and MnS precipitate.

Group V Cations
(Ca^{2+} Sr^{2+} and Ba^{2+})

calcium strontium barium

Reagent : $(NH_4Cl + NH_4OH) + (NH_4)_2CO_3$

These three metallic cations form soluble chlorides and sulfides and hence are separable from group 1, 2, 3 and 4 cations. However, their carbonates precipitate in a mixture of ammonium carbonate.

Group VI Cations
(NH_4^+, Mg^{2+}, K^+ and Na^+)

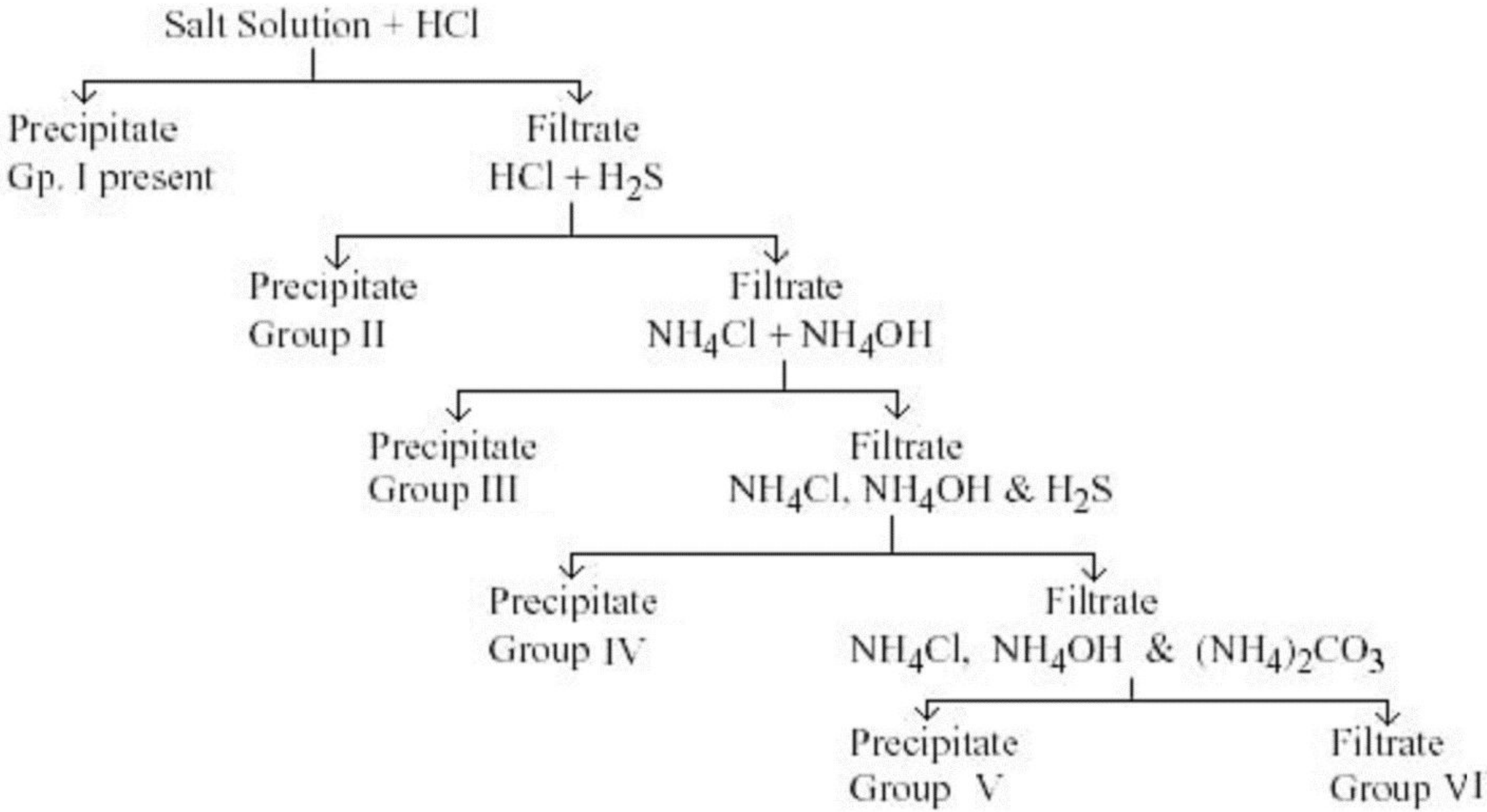
Ammonium magnesium potassium sodium

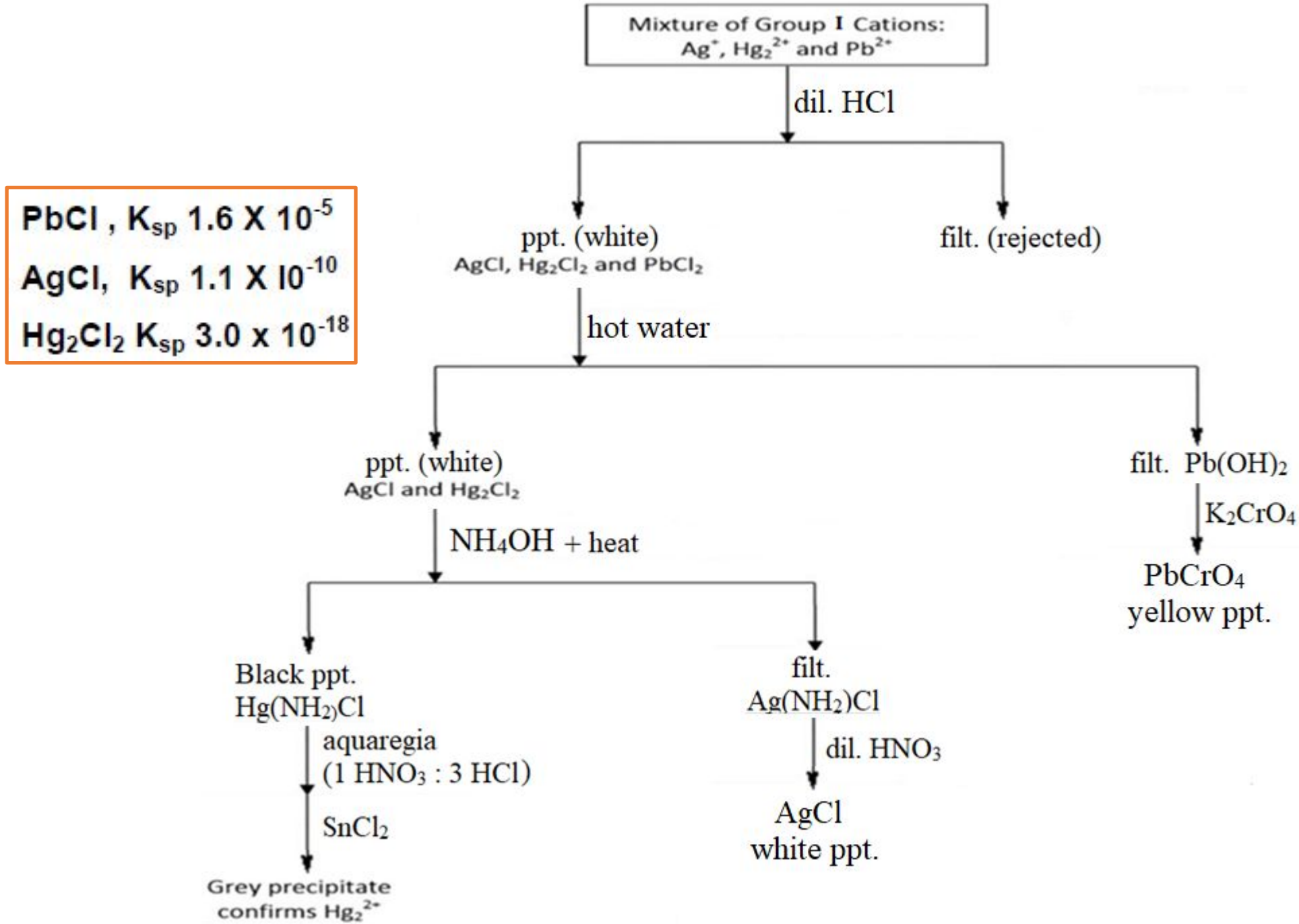
No specific reagent

None of the cations in this group form precipitates in the separation processes of group 1-5 cations and thus remain in the final solution.

Color	Inference
Blue or bluish green	Copper salts
Green	Nickel salts
Dark green	Chromium salts
Dark brown	Ferric salts
Light pink or flesh color	Manganese salts
Colorless	Absence of Cu^{2+}, Ni^{2+}, Fe^{3+}, Mn^{2+} and Co^{2+} salts

Systematic Separation of Cations in Qualitative Analysis





PbCl , K_{sp} 1.6 X 10^{-5}

AgCl, K_{sp} 1.1 X $I0^{-10}$

Hg_2Cl_2 K_{sp} 3.0 x 10^{-18}

Too large excess of the acid is avoided:

Dissolves the lead chloride by complex formation. Mercury (I) and silver chlorides do not dissolve because they are very unstable.

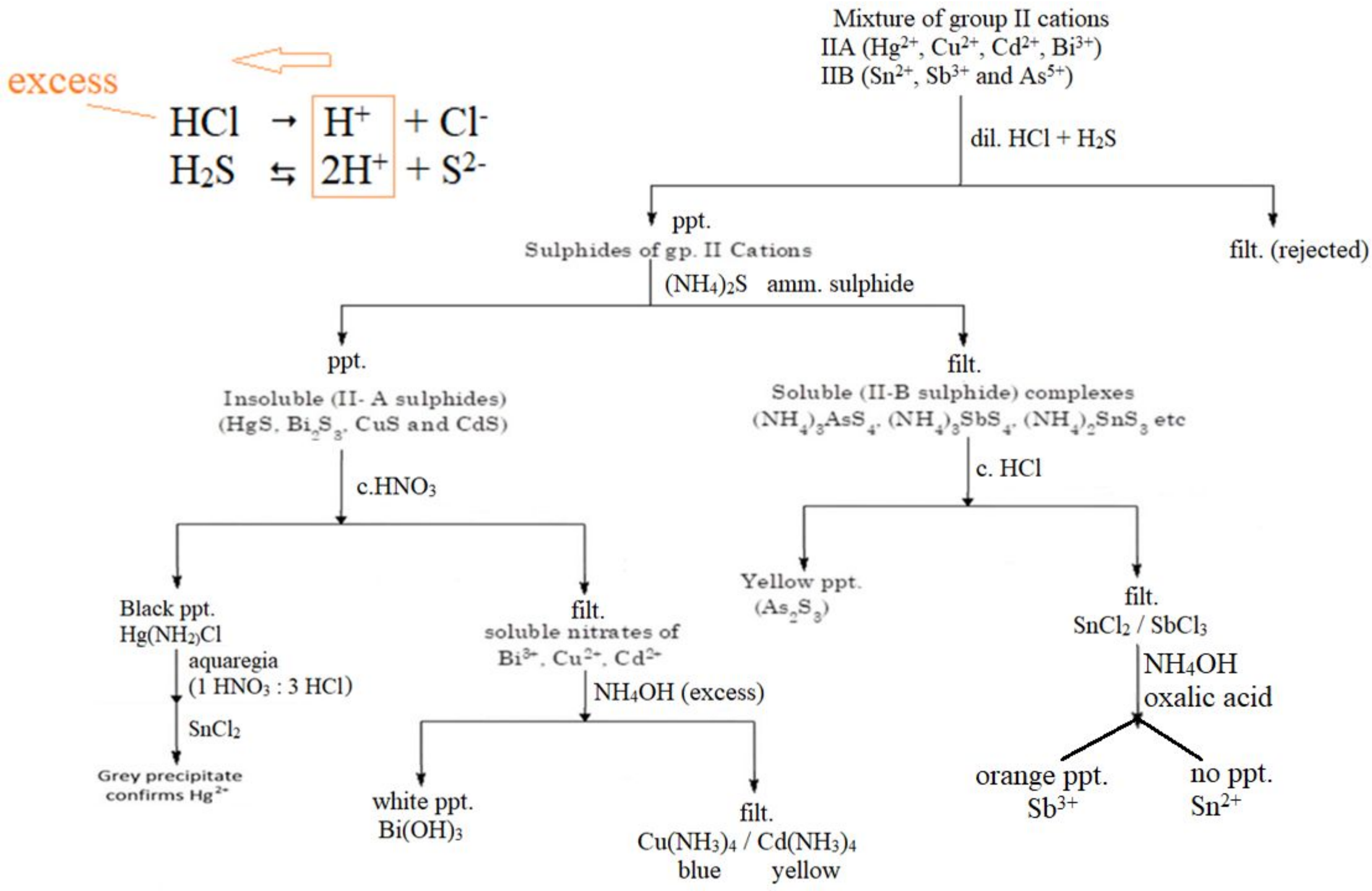
$$HCl \rightarrow H^+ + Cl^-$$

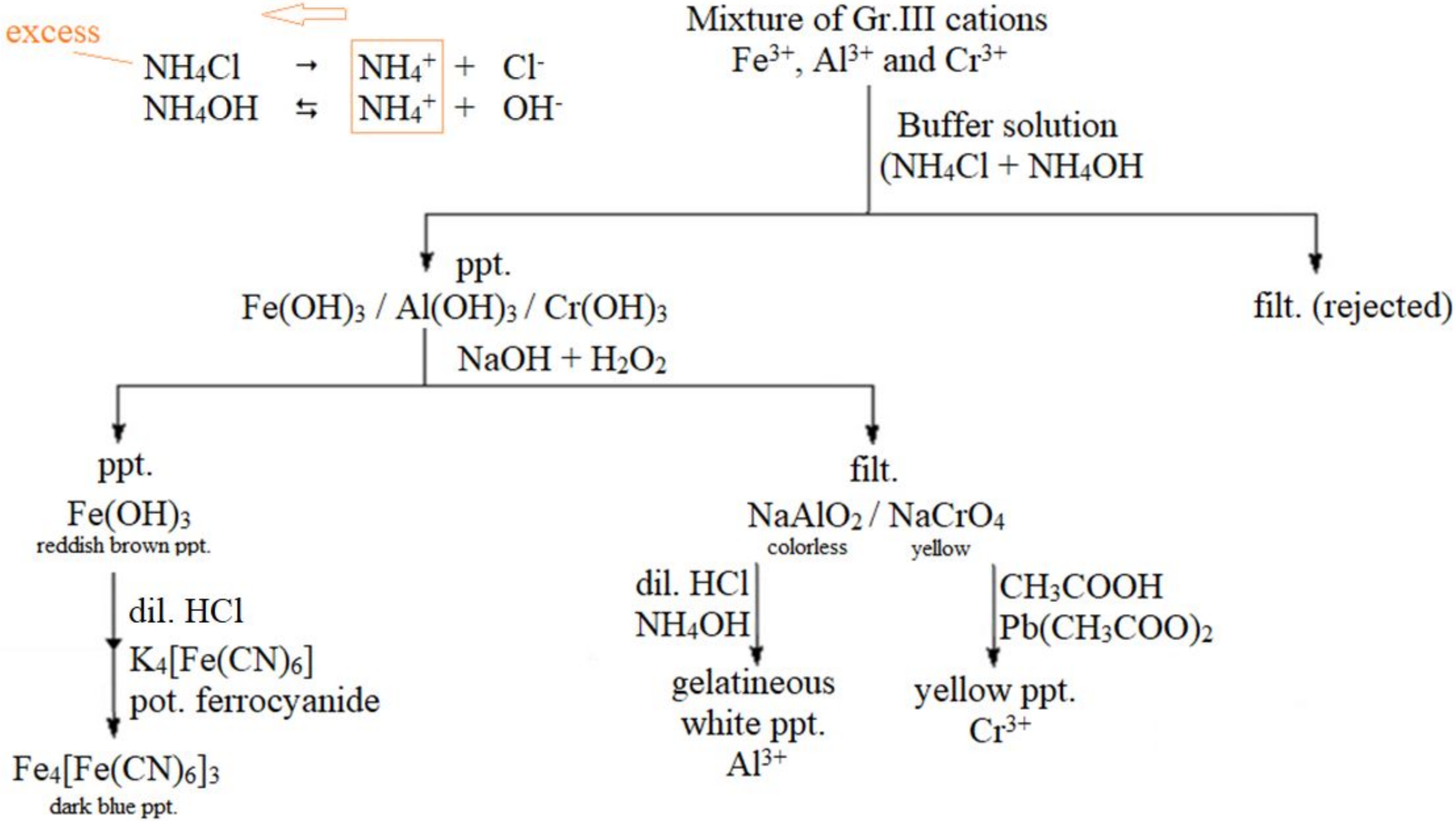
$$\downarrow PbCl_2 + Cl^- \leftrightarrows [PbCl_3]^- \quad \text{or} \quad [PbCl_4]^{2-}$$

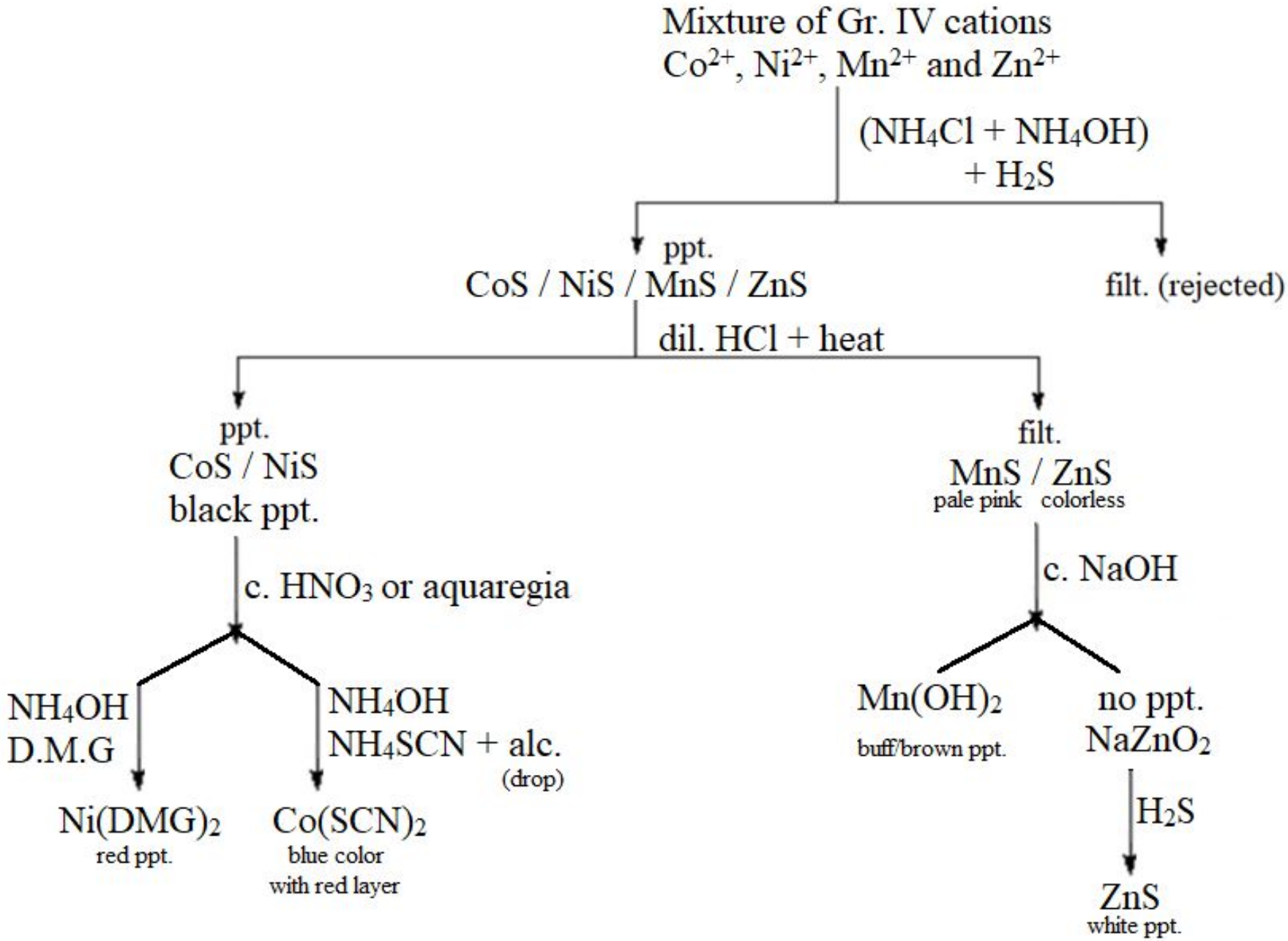
Large excess *Lead trichloride* *Lead tetrachloride*

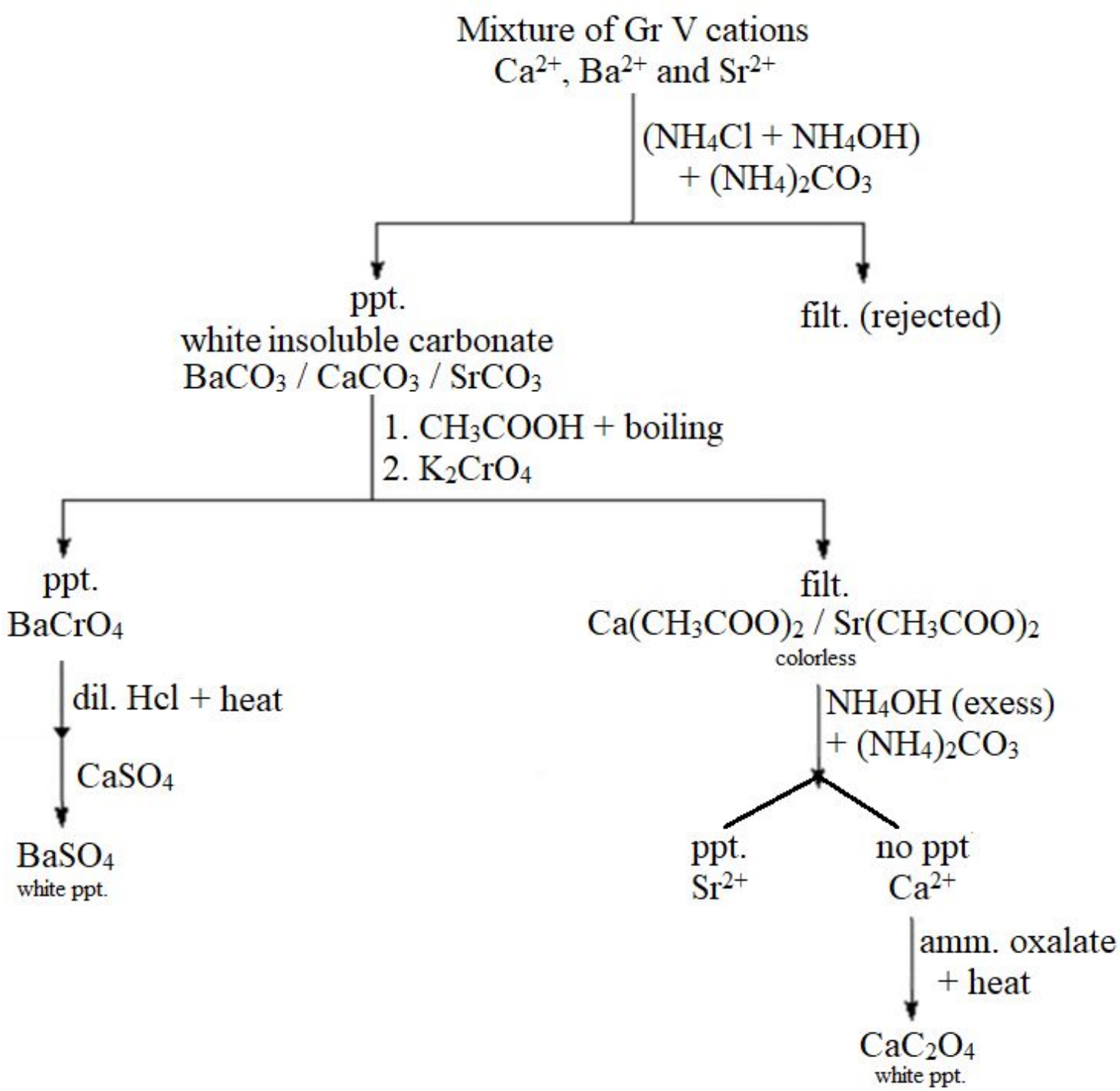
Soluble complexes

- Differentiate between mercuric and mercurous.?
- How can you separate and identify mixture of Hg_2^{2+}/ Hg^{2+}?


excess
HCl → H+ + Cl-
H2S ⇆ 2H+ + S2-
Mixture of group II cations
IIA (Hg2+, Cu2+, Cd2+, Bi3+)
IIB (Sn2+, Sb3+ and As5+)
dil. HCl + H2S
ppt.
Sulphides of gp. II Cations
filt. (rejected)
(NH4)2S amm. sulphide
ppt.
Insoluble (II- A sulphides)
(HgS, Bi2S3, CuS and CdS)
filt.
Soluble (II-B sulphide) complexes
(NH4)3AsS4, (NH4)3SbS4, (NH4)2SnS3 etc
c.HNO3
c. HCl
Black ppt.
Hg(NH2)Cl
aquaregia
(1 HNO3 : 3 HCl)
SnCl2
Grey precipitate
confirms Hg2+
filt.
soluble nitrates of
Bi3+, Cu2+, Cd2+
NH4OH (excess)
Yellow ppt.
(As2S3)
filt.
SnCl2 / SbCl3
NH4OH
oxalic acid
white ppt.
Bi(OH)3
filt.
Cu(NH3)4 / Cd(NH3)4
blue yellow
orange ppt.
Sb3+
no ppt.
Sn2+


excess
NH4Cl → NH4+ + Cl-
NH4OH ⇆ NH4+ + OH-
Mixture of Gr.III cations
Fe3+, Al3+ and Cr3+
Buffer solution
(NH4Cl + NH4OH
ppt.
Fe(OH)3 / Al(OH)3 / Cr(OH)3
filt. (rejected)
NaOH + H2O2
ppt.
Fe(OH)3
reddish brown ppt.
dil. HCl
K4[Fe(CN)6]
pot. ferrocyanide
Fe4[Fe(CN)6]3
dark blue ppt.
filt.
NaAlO2 / NaCrO4
colorless
yellow
dil. HCl
NH4OH
gelatineous
white ppt.
Al3+
CH3COOH
Pb(CH3COO)2
yellow ppt.
Cr3+


Mixture of Gr. IV cations
Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+}
$(NH_4Cl + NH_4OH) + H_2S$
ppt.
CoS / NiS / MnS / ZnS
filt. (rejected)
dil. HCl + heat
ppt.
CoS / NiS
black ppt.
filt.
MnS / ZnS
pale pink colorless
c. HNO_3 or aquaregia
c. NaOH
NH_4OH
D.M.G
NH_4OH
NH_4SCN + alc.
(drop)
$Mn(OH)_2$
buff/brown ppt.
no ppt.
$NaZnO_2$
$Ni(DMG)_2$
red ppt.
$Co(SCN)_2$
blue color
with red layer
H_2S
ZnS
white ppt.


Mixture of Gr V cations
Ca^{2+}, Ba^{2+} and Sr^{2+}
$(NH_4Cl + NH_4OH)$
$+ (NH_4)_2CO_3$
ppt.
white insoluble carbonate
$BaCO_3$ / $CaCO_3$ / $SrCO_3$
filt. (rejected)
1. CH_3COOH + boiling
2. K_2CrO_4
ppt.
$BaCrO_4$
filt.
$Ca(CH_3COO)_2$ / $Sr(CH_3COO)_2$
colorless
dil. Hcl + heat
$CaSO_4$
$BaSO_4$
white ppt.
NH_4OH (exess)
$+ (NH_4)_2CO_3$
ppt.
Sr^{2+}
no ppt
Ca^{2+}
amm. oxalate
+ heat
CaC_2O_4
white ppt.

Gr. VI cations

1. $NH_4^+ + c.\ NaOH + heat \longrightarrow NH_3$ gas forms white clouds when exposed to dil. HCl

   $NH_4^+ + Na_4[Co(NO_2)_6] \longrightarrow NH_4[Co(NO_2)_6]$ yellow ppt.

2. $Mg^{2+} + Buffer + Na_2HPO_4 \longrightarrow MgHPO_4$

   $MgHPO_4 \xrightarrow{NaOH} Mg(OH)_2$ white ppt.

3. $K^+ + Na_4[Co(NO_2)_6] \longrightarrow K_4[Co(NO_2)_6]$ yellow ppt.

   $K^+ \xrightarrow{\text{flame test}}$ violet

4. $Na^+ \xrightarrow{\text{flame test}}$ golden yellow

Scheme for separation of cations

HCl or a soluble chloride, preferably NH_4Cl, added to unknown; filtered

precipitate: contains chlorides of lead (Pb), silver (Ag), and mercurous mercury (Hg) $PbCl_2$ (white) AgCl (white) Hg_2Cl_2 (white) Group I	solution: H_2S passed into the acid solution; filtered			
	precipitate: treated with ammonium sulfide $(NH_4)_2S$; filtered		solution: neutralized with NH_4OH and NH_4Cl; filtered	
	precipitate: contains cupric (black) cadmium (yellow) bismuth (brown) and mercuric (black) sulfides Group IIa	solution: contains arsenic, antimony, and tin cations Group IIb	precipitate: contains aluminum (Al), chromium (Cr), and ferric (Fe) hydroxides $Al(OH)_3$ (white) $Cr(OH)_3$ (gray-green) $Fe(OH)_3$ (brown) Group III	solution: H_2S passed into alkaline solution; filtered
				precipitate: contains cobalt (Co), nickel (Ni), manganese (Mn), and zinc (Zn) sulfides CoS (black) NiS (black) MnS (buff) ZnS (white) Group IV
				solution: NH_4OH and NH_4Cl and $(NH_4)_2CO_3$ added; filtered
				precipitate: barium, strontium, and calcium carbonates (all white) Group V
				solution: contains magnesium, sodium, and potassium ions Group VI

Report

- **Physical Properties**

Colour	

- **Chemical Properties**

Experiment	Observation	Result

Experiment	Observation	Result

The cations are ..... & .....