Analysis of cations

Analysis of metallic elements in compounds or samples is an integral part of chemical research. The purpose of this experiment is to learn the techniques to separate and identify some common cations and to understand the principles for the equilibria of precipitation and complex formation. The systematic analysis of cations is an integral part of the salt analysis (or systematic qualitative analysis).

Aim

To identify the cationic radicals 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 behaviour of the cations toward a set of common test reagents differs from one cation to another and furnishes the basis for their separation.

The qualitative analysis of an inorganic mixture is started by first carrying out some preliminary tests. The Preliminary tests for cations are

1. **Physical examination**
2. **Charcoal cavity test**
3. **Boraxbead test**
4. **Flame test**

These tests do not give conclusive evidence yet they provide some information about the ions present in the mixture.

Qualitative analysis of cations usually consists of three stages.

1. *First* based on different solubility properties the cations are separated into 5 groups through the successive addition of selective precipitating reagents.
2. *Second*, within each group precipitated cations are separated through selective dissolution processes.
3. *Third*, the presence of each cation is verified through different identification tests.

The cations are classified into the following 5 groups.

1. Group I Cations (Ag^{+}, Hg_2^{2+} and Pb^{2+} – insoluble chlorides):

Among the common metallic cations only three cations form insoluble chlorides with hydrochloric acid. When 6M of HCl is added to the solution, white precipitates of AgCl, Hg_2Cl_2 and $PbCl_2$ are formed. Other metallic cations remain in solution.

2. Group II Cations (Hg2+, Pb2+, Cu2+, Bi3+, Cd2+, As3+, Sb3+ and Sn4+ – insoluble sulphides in acidic medium):

After the insoluble chlorides are isolated, the pH of the solution is adjusted to 0.5 and then H_2S is added. Since the concentration of sulphide ion (s^{2-}) is very low at low pH, only those metallic sulphided having very low Ksp values will precipitate. Cations with larger Ksp values for their sulphides remain in solution.

3. Group III Cations (Al^{3+}. Fe^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Zn^{2+} and Mn^{2+} – insoluble sulphides or hydroxides in alkaline medium):

After isolating the insoluble sulphides in acidic medium, the solution is made basic and the metallic sulphides having larger Ksp values such as ZnS, NiS, CoS and MnS precipitate. Moreover, since the solution is basic Al^{3+}, Fe^{3+} and Cr^{3+} form insoluble hydroxides and are also separated from the solution.

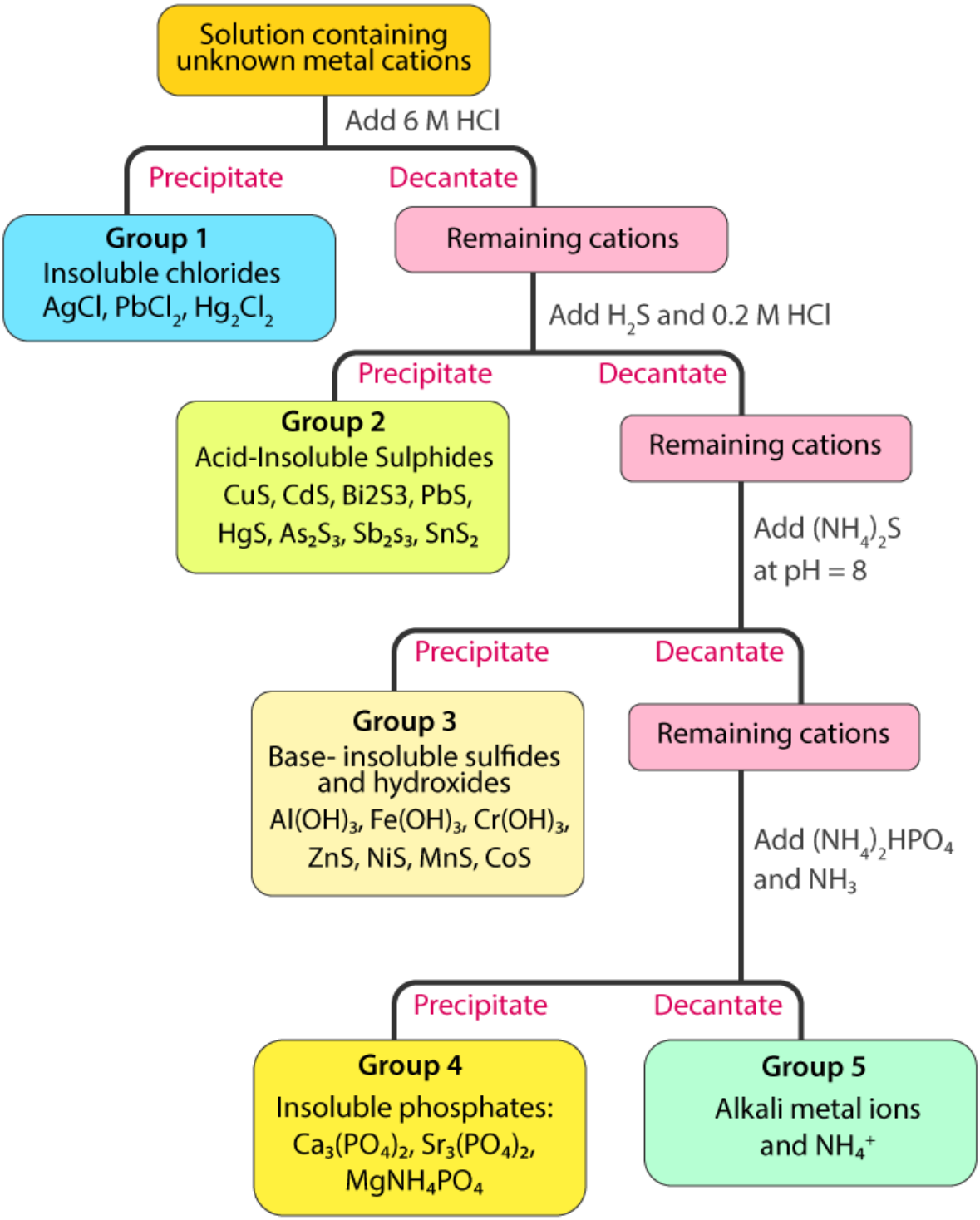
4. Group IV Cations (Ca^{2+}, Sr^{2+} and Ba^{2+} – carbonate precipitates):

These three metallic cations all belong to Group IIA in the periodic table of elements and therefore their chemical properties are very similar. They form soluble chlorides and sulphides and hence are separable from groups 1, 2 and 3 cations. However, their carbonates precipitate in a mixture of ammonium carbonate, ammonium chloride or ammonia solution.

5. Group V Cations (Mg^{2+}, Na^{+}, K^{+} and NH_4^{+}):

None of the cations in this group form precipitates in the separation processes of group 1-4 cations and thus remain in the final solution.

The flowchart for separating the five groups of cations is given below.


Solution containing unknown metal cations
Add 6 M HCl
Precipitate
Decantate
Group 1
Insoluble chlorides
AgCl, PbCl2, Hg2Cl2
Remaining cations
Add H2S and 0.2 M HCl
Precipitate
Decantate
Group 2
Acid-Insoluble Sulphides
CuS, CdS, Bi2S3, PbS,
HgS, As2S3, Sb2s3, SnS2
Remaining cations
Add (NH4)2S
at pH = 8
Precipitate
Decantate
Group 3
Base- insoluble sulfides and hydroxides
Al(OH)3, Fe(OH)3, Cr(OH)3,
ZnS, NiS, MnS, CoS
Remaining cations
Add (NH4)2HPO4
and NH3
Precipitate
Decantate
Group 4
Insoluble phosphates:
Ca3(PO4)2, Sr3(PO4)2,
MgNH4PO4
Group 5
Alkali metal ions
and NH4+