

7.8: Qualitative Cation Analysis

Learning Objectives

- To know how to separate metal ions by selective precipitation.
- To understand how several common metal cations can be identified in a solution using selective precipitation.

The composition of relatively complex mixtures of metal ions can be determined using **qualitative analysis**, a procedure for discovering the identity of metal ions present in the mixture (rather than quantitative information about their amounts). The procedure used to separate and identify more than 20 common metal cations from a single solution consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively less selective until almost all of the metal ions are precipitated, as illustrated in Figure 7.8.1.

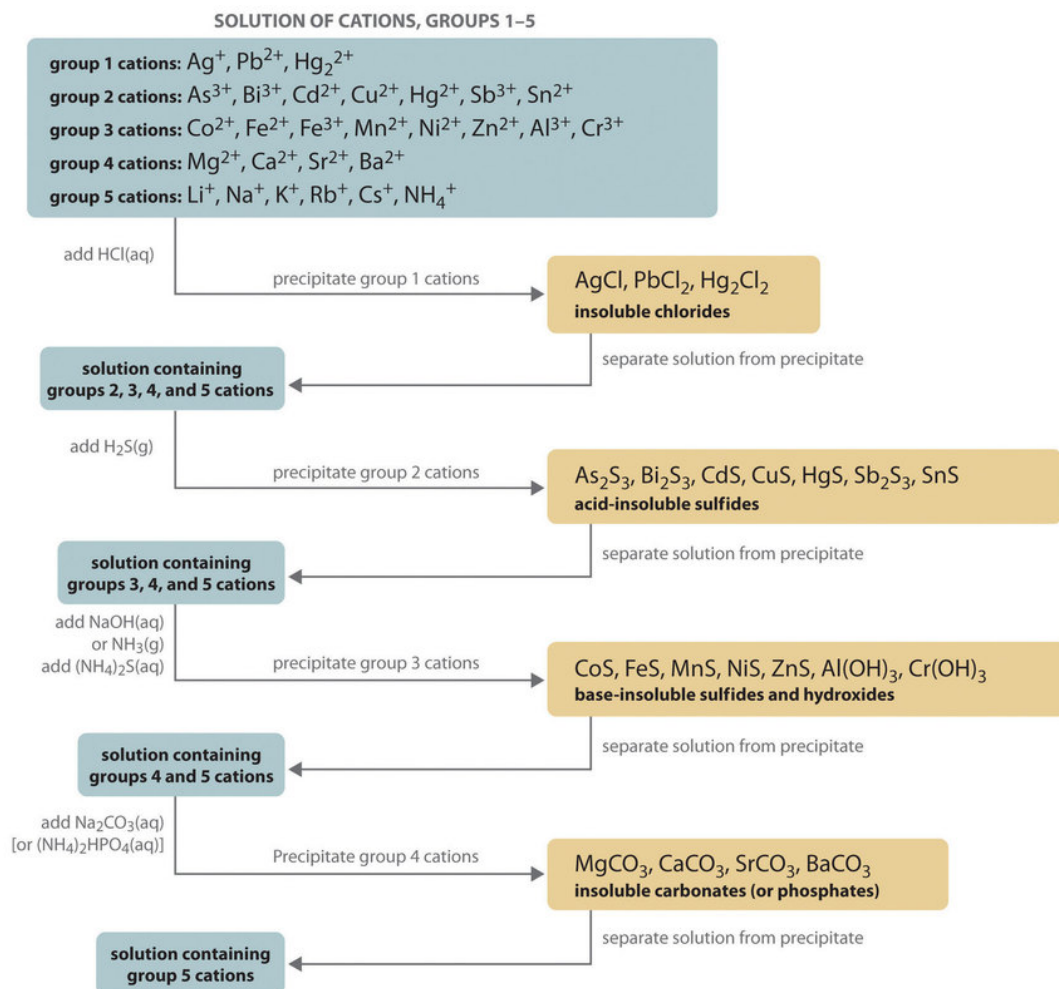


Figure 7.8.1: Steps in a Typical Qualitative Analysis Scheme for a Solution That Contains Several Metal Ions

Group 1: Insoluble Chlorides

Most metal chloride salts are soluble in water; only Ag^+ , Pb^{2+} , and Hg_2^{2+} form chlorides that precipitate from water. Thus the first step in a qualitative analysis is to add about 6 M HCl, thereby causing AgCl , PbCl_2 , and/or Hg_2Cl_2 to precipitate. If no precipitate forms, then these cations are not present in significant amounts. The precipitate can be collected by filtration or centrifugation.

Group 2: Acid-Insoluble Sulfides

Next, the acidic solution is saturated with H_2S gas. Only those metal ions that form very insoluble sulfides, such as As^{3+} , Bi^{3+} , Cd^{2+} , Cu^{2+} , Hg^{2+} , Sb^{3+} , and Sn^{2+} , precipitate as their sulfide salts under these acidic conditions. All others, such as Fe^{2+} and Zn^{2+} , remain in solution. Once again, the precipitates are collected by filtration or centrifugation.

Group 3: Base-Insoluble Sulfides (and Hydroxides)

Ammonia or NaOH is now added to the solution until it is basic, and then $(\text{NH}_4)_2\text{S}$ is added. This treatment removes any remaining cations that form insoluble hydroxides or sulfides. The divalent metal ions Co^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , and Zn^{2+} precipitate as their sulfides, and the trivalent metal ions Al^{3+} and Cr^{3+} precipitate as their hydroxides: $\text{Al}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$. If the mixture contains Fe^{3+} , sulfide reduces the cation to Fe^{2+} , which precipitates as FeS .

Group 4: Insoluble Carbonates or Phosphates

The next metal ions to be removed from solution are those that form insoluble carbonates and phosphates. When Na_2CO_3 is added to the basic solution that remains after the precipitated metal ions are removed, insoluble carbonates precipitate and are collected. Alternatively, adding $(\text{NH}_4)_2\text{HPO}_4$ causes the same metal ions to precipitate as insoluble phosphates.

Group 5: Alkali Metals

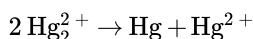
At this point, we have removed all the metal ions that form water-insoluble chlorides, sulfides, carbonates, or phosphates. The only common ions that might remain are any alkali metals (Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+) and ammonium (NH_4^+). We now take a second sample from the original solution and add a small amount of NaOH to neutralize the ammonium ion and produce NH_3 . (We cannot use the same sample we used for the first four groups because we added ammonium to that sample in earlier steps.) Any ammonia produced can be detected by either its odor or a litmus paper test. A flame test on another original sample is used to detect sodium, which produces a characteristic bright yellow color. The other alkali metal ions also give characteristic colors in flame tests, which allows them to be identified if only one is present.

Metal ions that precipitate together are separated by various additional techniques, such as forming complex ions, changing the pH of the solution, or increasing the temperature to redissolve some of the solids. For example, the precipitated metal chlorides of group 1 cations, containing Ag^+ , Pb^{2+} , and Hg_2^{2+} , are all quite insoluble in water. Because PbCl_2 is much more soluble in hot water than are the other two chloride salts, however, adding water to the precipitate and heating the resulting slurry will dissolve any PbCl_2 present. Isolating the solution and adding a small amount of Na_2CrO_4 solution to it will produce a bright yellow precipitate of PbCrO_4 if Pb^{2+} were in the original sample (Figure 7.8.2).

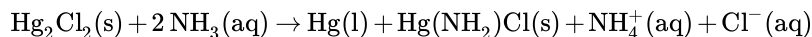


Figure 7.8.2: When a small amount of Na_2CrO_4 solution is added to a sample containing Pb^{2+} ions in water, a bright yellow precipitate of PbCrO_4 forms. (CC BY-SA 3.0 Unported; [PRHaney](#) via [Wikipedia](#)).

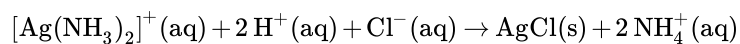
As another example, treating the precipitates from group 1 cations with aqueous ammonia will dissolve any AgCl because Ag^+ forms a stable complex with ammonia: $[\text{Ag}(\text{NH}_3)_2]^+$. In addition, Hg_2Cl_2 [disproportionates](#) in ammonia.



to form a black solid that is a mixture of finely divided metallic mercury and an insoluble mercury(II) compound, which is separated from solution:



Any silver ion in the solution is then detected by adding HCl , which reverses the reaction and gives a precipitate of white AgCl that slowly darkens when exposed to light:



Similar but slightly more complex reactions are also used to separate and identify the individual components of the other groups.

Summary

In qualitative analysis, the identity, not the amount, of metal ions present in a mixture is determined. The technique consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively less selective until almost all the metal ions are precipitated. Other additional steps are needed to separate metal ions that precipitate together.

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