SEPARATION AND IDENTIFICATION OF A MIXTURE OF CATIONS

Introduction

This laboratory exercise will introduce you to the area known as qualitative analysis. Unlike quantitative analysis, which is strictly concerned with the *amount* of a given ion in solution, qualitative analysis is concerned with *identification* of various chemical species present in a mixture.

Very often qualitative analysis is used to identify mixtures of metal ions. The mixture that you will be working with contains Ba^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, and Cu^{2+}. Based upon previous laboratory experience, you may already have learned to recognize these ions based on the color of the resulting solution. For example, Ni^{2+} is pale green, Co^{2+} is pink, Fe^{3+} is usually yellow, and Mn^{2+} is either colorless or very pale pink, depending upon the concentration. Most of the tests for these ions involve the precipitation of the ion with a specific reagent (as is the case of with Ca^{2+} and Ba^{2+}) or the formation of a colored precipitate or complex ion (as is the case with Ni^{2+} and Fe^{3+}). Some of these tests are listed below

Cu^{2+}: look for the formation of a deep-blue solution with NH_3

Ni^{2+}: add dimethylgloxime (DMG); look for a red precipitate

Fe^{3+}: add KSCN, look for a blood-red color

Mn^{2+}: oxidize to MnO_4^-, look for the purple color of this ion

Ba^{2+}: add SO_4^{2-} and look for a precipitate of $BaSO_4$

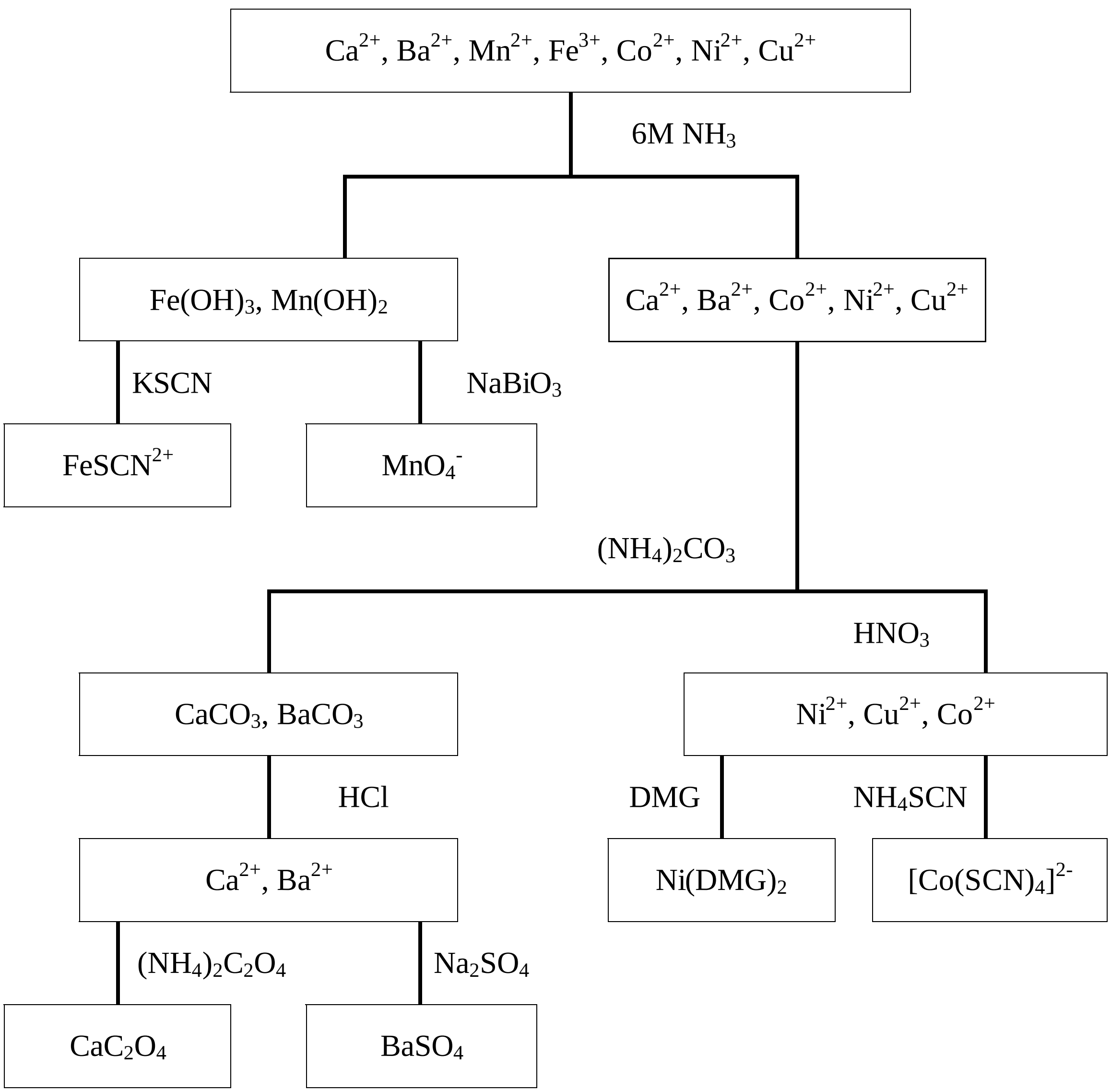
Ca^{2+}: add $C_2O_4^{2-}$ and look for a precipitate of CaC_2O_4

If given to you individually, you could probably identify each of the above ions based either on either a visual inspection or a simple chemical test. However, your unknown will contain a mixture of these ions. The problem with a mixture of ions is that the color of one ion will very often mask the color of another. For example, the color of Mn^{2+} is so pale that it can be obscured by any of the other ions. Similarly, the chemical tests for the ions may also be masked by the presence of other ions. Therefore the chemical properties of the ions, most notably solubility, will be used to separate the ions.

There are a variety of qualitative analysis schemes for separating mixtures of metal ions. The requirement is a reagent, or series of reagents, that will precipitate some, but not all, of the metal ions. Nearly all of the transition metal ions form insoluble sulfides, and most qualitative analysis schemes begin with adding a source of sulfide to the mixture. However, sulfides are toxic, and we will therefore avoid using them in this laboratory. Some metal ions form insoluble hydroxides and can be precipitated from basic solution; Mn^{2+} and Fe^{3+} fall into this category. Additionally, some metal ions form insoluble carbonates and can be precipitated with a source of the carbonate ion; Ca^{2+} and Ba^{2+} are ions that fall into this category.

The first step of the procedure we will employ involves precipitation of Mn^{2+} and Fe^{3+} as hydroxides, separating them from the rest of the mixture. Next, the resulting solution is reacted with ammonium carbonate, which precipitates any Ba^{2+} and Ca^{2+} present as $BaCO_3$ and $CaCO_3$. Finally, this leaves the ions Co^{2+}, Cu^{2+}, and Ni^{2+} in solution. These ions should not interfere with each other, and the presence of these ions can be confirmed with simple chemical tests.

A flowchart for this procedure is shown below.



Procedure

1.Start with a small test tube approximately half full of your unknown solution. Add one drop of 6M HNO_3, followed by 1 mL (approximately 20 drops) of 6M NH_3. If present in your unknown, a precipitate of $Fe(OH)_3$ and $Mn(OH)_2$ will form.

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

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

Centrifuge the mixture and transfer the solution to a second test tube.

Caution: *a centrifuge must always be balanced; never place a single test tube in a centrifuge. If there are no other samples, balance the centrifuge with a second test tube containing a roughly equivalent volume of water. A centrifuge can be balanced with two, three, four, or six test tubes.*

Caution: *do not in any way attempt to use your hands to stop a spinning centrifuge. Allow the centrifuge to spin down without outside assistance.*

2. Add 2 mL (approximately 40 drops) of 1 M $(NH_4)_2CO_3$ to solution from part 1 and shake or stir the contents. If present in your unknown, a precipitate of $CaCO_3$ and $BaCO_3$ will form.

$$Ba^{2+} + CO_3^{2-} \rightarrow BaCO_3$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

Centrifuge the mixture and transfer the solution to a third test tube.

3. To the precipitate from part 1 ($Fe(OH)_3$ and $Mn(OH)_2$) add 6M HNO_3 dropwise until the precipitate dissolves. This merely redissolves the precipitates, giving the Mn^{2+} and Fe^{3+} ions in solution.

$$Mn(OH)_2 + 2H_3O^+ \rightarrow Mn^{2+} + 2H_2O$$

$$Fe(OH)_3 + 3H_3O^+ \rightarrow Fe^{3+} + 3H_2O$$

Next, add 2 mL of deionized water. Divide the contents of this test tube into two portions. To the first part, add a few drops of KSCN solution. The formation of a blood-red solution confirms the presence of Fe^{3+}.

$$Fe^{3+} + SCN^- \rightarrow FeSCN^{2+}$$

To the second portion of the solution, add a very small portion of sodium bismuthate, $NaBiO_3$. This is a powerful oxidizing agent, and oxidizes the Mn^{2+} ion (which is nearly colorless) to the MnO_4^- (which is purple in color.)

$$2Mn^{2+} + 5BiO_3^- + 14H^+ \rightarrow 2MnO_4^- + 5Bi^{3+} + 7H_2O$$

Note: the test for manganese can be problematic. If you add too much $NaBiO_3$, it will mask the color of the permanganate ion. You want to add a very small amount of this reagent. If nothing seems to happen, tilt the test tube sideways and add the $NaBiO_3$ to the top of the test tube. Tilt the tube enough to moisten the $NaBiO_3$ with the solution, and allow a few drops of 6M HNO_3 to run down over the wet sodium bismuthate. If Mn^{2+} is present you should see the development of a purple color around the edges of the solid.

4. To the solid from part 2 ($BaCO_3$, $CaCO_3$) slowly add 6M HCl until the precipitate is dissolved. Add just enough to dissolve the precipitate. What do you observe upon the addition of the HCl?

$$BaCO_3 + H_3O^+ \rightarrow Ba^{2+} + CO_2 + H_2O$$

$$CaCO_3 + H_3O^+ \rightarrow Ca^{2+} + CO_2 + H_2O$$

Add 1 mL (approximately 20 drops) of 1M Na_2SO_4 and stir the solution. If Ba^{2+} is present, a white precipitate of $BaSO_4$ should form. Centrifuge the mixture and decant the liquid into a clean test tube (you may omit this step if no precipitate is present). Add 3 drops of 6M NH_3 and add 1 mL of 0.30 M $(NH_4)_2C_2O_4$. Stir and let stand for a few minutes. If Ca^{2+} is present in your unknown a white precipitate of CaC_2O_4 should form.

5. The solution form step 2 contains the ions Co^{2+}, Cu^{2+}, and Ni^{2+}, if present in your unknown. The color of the solution itself may give some indication of the ions present. Recall that the Ni^{2+} ion is green, and the Co^{2+} ion is pink. Ordinarily, the Cu^{2+} ion is pale blue in color. However, due to the ammonia added in previous steps, it is most likely present as the $[Cu(NH_3)_4]^{2+}$ ion, which is deeper blue in color.

Transfer this solution to a small (50-mL) beaker and evaporate gently to dryness on a hot plate. The purpose of this step is to drive off the ammonia added in previous steps. Reconstitute the solid by adding approximately 1 mL of 1 M H_3PO_4 and 2 mL of Na_2HPO_4. Divide the resulting solution into three portions.

1. To the first test tube add a few drops of 6M NH_3 (to ensure that the solution is basic), followed by a few drops of dimethylgloxime (DMG) solution. A red precipitate of $Ni(DMG)_2$ confirms the presence of nickel.

2. To the second test tube add approximately 10-20 drops of saturated ammonium thiocyanate (NH_4SCN) in ethanol. Do not shake or mix the contents of the test tube. If Co^{2+} is present, the complex ion $[Co(SCN)_4]^{2-}$ will form, which imparts a blue color to the ethanol layer.

3. To the third test tube, add approximately 10-20 drops of 6M NH_3. If the color of the solution changes to a deep blue, Cu^{2+} is present.

Laboratory Report	Name:

Unknown Number:

Indicate with a “present” or “not present” whether each of the following ions was in your unknown. For ions that were present in your unknown, write a balanced chemical equation for the chemical test that you used to identify the ion.

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Ca^{2+}

Mn^{2+}

Fe^{3+}

Co^{2+}

Ni^{2+}

Cu^{2+}

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