I. QUALITATIVE ANALYSIS OF CATIONS

Note that the following directions are written for a "known" solution (a standard) that contains all of the cations. An "unknown" solution (a sample) will not form all of the products described in the procedure. Make note of any differences in the "unknown" solution as it is analyzed. In the directions that follow, a description of the physical properties and the chemistry of the substances appears in boxed frames:

Aqueous solutions of Ag^{+} and Zn^{2+} are colorless. Aqueous solutions of Fe^{3+} is often yellowish due to hydrolysate of $Fe(OH)_3$; Cu^{2+} is light blue in aqueous solutions.

1. Separation of the Silver from Iron, Copper, and Zinc Ions.

Most chloride salts are soluble; however, Ag^{+} ions form an insoluble chloride. These Ag^{+} ions can be separated from the other ions present in this qualitative analysis scheme by precipitating them as chlorides. All of the other ions will stay in solution.

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$$

a. Add 8 drops of 10% HCl to approx. **5 ml** of the solution to be analyzed. Stir. A white precipitate indicates that the Ag^{+} ion is present.
b. Test to be sure that precipitation is complete by adding one more drop of 10% HCl. No additional precipitate should form. If more precipitate does form, continue adding 10% HCl until precipitation is complete.
c. Filtrate the solution to quantitatively remove AgCl.
d. Save the precipitate on the filtration paper **for procedure #2.**
e. Save the clear liquid (filtrate) into a second test tube **for procedure# 3**.

2. Confirmation of Ag(+).

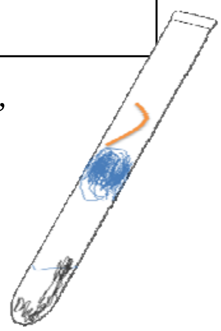
When 2 M NH_3 is added to AgCl, the Ag^{+} ion forms a colorless complex ion and goes into solution: $AgCl_{(s)} + 2\ NH_{3(aq)} \Leftrightarrow Ag(NH_3)_2^{+}(aq) + Cl^{-}(aq)$ *Addition of hydrochloric acid to the $Ag(NH_3)^{2+}$ complex ion breaks apart the ion. The NH_3 combines with H^{+} to form NH_4^{+}, and the Ag^{+} ion recombines back with the Cl^{-} ion to precipitate as white AgCl.* $Ag(NH_3)_2^{+}{}_{(aq)} + Cl^{-}_{(aq)} + 2\ H^{+}_{(aq)} \Leftrightarrow AgCl_{(s)} + 2\ NH_4^{+}{}_{(aq)}$

a. Load (with a spatula) the precipitate from procedure 1*d*, which is AgCl, to a clean test tube and add 1 mL 2 M NH_3.
b. Stir until the precipitate completely dissolves.
c. Add 15 drops of 10% HCl to the solution. The solution will smoke and the reaction between the strong acid and the base will give off heat whether or not silver is present. The test tube may get very warm.
d. Stir and test with pH indicator paper to be sure the solution is acidic. If it is not acidic, add more HCl. The reappearance of the white AgCl precipitate in the acidic solution confirms the presence of Ag(+).

3. Separation of Iron and Copper from Zinc. Confirmation of ammonium.

In a basic solution, the amphoteric zinc will form a colorless complex ion and remain in solution, while the hydroxides of all the other ions will precipitate. The iron will precipitate as rust colored $Fe(OH)_3$, and the copper as blue $Cu(OH)_2$. The reactions are as follows:

$$Fe^{3+}{}_{(aq)} + 3\ OH^-{}_{(aq)} \rightarrow Fe(OH)_{3(s)}$$
$$Cu^{2+}{}_{(aq)} + 2\ OH^-{}_{(aq)} \rightarrow Cu(OH)_{2(s)}$$
$$Zn^{2+}{}_{(aq)} + 4\ OH^-{}_{(aq)} \rightarrow Zn(OH)_4{}^{2-}{}_{(aq)}$$



a. Put 1 ml of the solution saved from procedure 1*e* in a test tube and add 2 M NaOH, until the solution is basic and then add 3 more drops. Place a small paper plug loosely about halfway down the test tube, but **not** touching the solution (see Figure). Hang a piece of watered pH paper in the tube so that the bottom of the paper is on the plug and not touching the solution (otherwise it will turn deep blue!). HEAT carefully the test tube. If ammonia is present, it will be released and color the pH paper dark green. $NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow NH_{3\ (g)} + H_2O$
b. To the rest of the solution saved from procedure 1*e* add NaOH, and observe a precipitate indicating the presence of either copper or iron or both. Heat the testube carefully over a burner so that the precipitation is complete.
c. Filtrate the solution to separate the clear solution from the solid. Save the clear solution, which may contain $Zn(OH)_4{}^{2-}$ ions for **procedure #6.**
d. Wash the precipitate with a mixture of 10 drops of 10% NaOH and 10 drops of water.
e. Save the precipitate for **procedure #4.**

4. Separation of Iron from Copper; Confirmation of Cu(2+).

Both cupric hydroxide, $Cu(OH)_2$, and ferric hydroxide, $Fe(OH)_3$, readily dissolve in acid solution.

$$Cu(OH)_{2(s)} + 2\ H^+{}_{(aq)} \rightarrow Cu^{2+}{}_{(aq)} + 3\ H_2O_{(l)}$$
$$Fe(OH)_{3(s)} + 3\ H^+{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + 3\ H_2O_{(l)}$$

Aqueous ammonia added to a solution in which Cu^{2+} is present, will cause the deep blue tetraammine copper(II) complex ion to form. The presence of this deep blue color confirms the presence of copper. At the same time, the basic ammonia solution will precipitate the hydroxides of iron.

$$Cu^{2+}{}_{(aq)} + 4\ NH_{3(aq)} \Leftrightarrow Cu(NH_3)_4{}^{2+}{}_{(aq)}$$
$$Fe^{3+}{}_{(aq)} + 3\ OH^-{}_{(aq)} \rightarrow Fe(OH)_{3(s)}$$

An additional and sensitive confirmatory test for copper is to precipitate the red-brown copper(II) hexacyanoferrate(II) [also called copper(II) ferrocyanide], $Cu_2[Fe(CN)_6]_{(s)}$, from a Cu^{2+} solution.

a. To the precipitate from procedure 3*e*, add 5 drops of deionized water.
b. Add 35% H_2SO_4 dropwise until the solution is acidic when tested with pH paper (about 6 drops). Stir to dissolve precipitate.
c. To the solution, add 2 M aqueous NH_3 until the solution is basic (pH paper), and then add 1 mL extra.
d. Separate the supernatant liquid from the precipitate by filtration. Save the precipitate for **procedure #5**. The presence of the deep blue $[Cu(NH_3)_4]^{2+}$ ion is the confirmatory test for copper.
e. For an additional confirmatory test, to the solution containing the $Cu(NH_3)_4^{2+}$ add 50% CH_3COOH, acetic acid, until the deep blue color fades and the solution becomes acidic. Then add 2 drops of 10% $K_4[Fe(CN)_6]$. A red-brown precipitate of $Cu_2[Fe(CN)_6]$ reconfirms the presence of Cu(2+).

5. Confirmation of Fe(3+).

Ferric hydroxide will dissolve in sulfuric acid. Addition of the thiocyanate ion, SCN^-, forms a deep wine-red colored complex ion with iron that is a very sensitive test for the presence of iron.

$$Fe(OH)_{3(s)} + 3\,H^+_{(aq)} \rightarrow Fe^{3+}_{(aq)} + 3\,H_2O_{(l)}$$
$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \Leftrightarrow FeSCN^{2+}_{(aq)}$$

a. Wash the precipitate of iron hydroxides from procedure 4*d*.
b. Add 35% H_2SO_4 dropwise until the precipitate dissolves.
c. To the solution add 5 drops of 15% NH_4SCN solution. The deep red $FeSCN^{2+}$ ion confirms the presence of Fe(3+).

6. Confirmation of Zn(2+).

*The confirmatory test for zinc is the formation of a precipitate of potassium zinc hexacyanoferrate(II), $K_2Zn_3[Fe(CN)_6]_2$. This precipitate is nearly **white** if pure, but if a **trace of iron** is present, it may appear light green or blue-green in color. It might also appear as a <u>suspension</u>, a jelly-like precipitate that is suspended in solution, rather than sinking to the bottom.*

$$[Zn(NH_3)_4]^{2+}_{(aq)} + 4\,H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + NH_4^+{}_{(aq)}$$
$$3\,Zn^{2+}_{(aq)} + 2\,K^+_{(aq)} + 2\,[Fe(CN)_6]^{4-}_{(aq)} \rightarrow K_2Zn_3[Fe(CN)_6]_{2(s)}$$

a. If your solution from procedure *3c* contains Zn^{+2}, it will be complexed with OH^- as $Zn(OH)_4^{2-}$
b. Make the solution from procedure 3*c* slightly acidic by adding 10% HCl dropwise.
c. Add 3 drops of 10% $K_4[Fe(CN)_6]$ and stir.
d. Check the confirmatory precipitate of $K_2Zn_3[Fe(CN)_6]_2$ which will be white to light green or blue green in color.
e. Dispose of the zinc precipitate.

7. Repeat steps 1–6 for the cation in your unknown sample. Be sure to record the results for each step.

SAMPLE = 2 cations

CATION ANALYSIS DATA TABLE

		Known Solution		Unknown Solution	
Step	**Procedure**	**Results**	**Conclusion**	**Results**	**Conclusion**
1					
2					
3					
4					
5					
6					

Qualitative Analysis of Cations