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Experiment #11 – Qualitative Analysis Scheme of Main Group and Transition Metal Cations*

The following experiment is intended to continue the introduction of qualitative analysis through the identification of various main group and transition metal cations. Recall that the analysis of a substance can be extremely difficult given the fact that there are thousands of possibilities for reactions with some similar results. For example, you may have seen from the Group I qualitative analysis that Ag^{+}, Pb^{+2}, and Hg_2^{+2} all produce a white precipitate when Cl^{-} is added.

In this experiment, the ions initially chosen were limited to aluminum, the alkaline earth metals, and certain first-row transition metals with the goal of minimizing the amount of hazardous waste generated. Analysis of both a known and unknown solution will test for Al^{+3}, Ba^{+2}, Ca^{+2}, Co^{+2}, Cu^{+2}, Fe^{+3}, Mg^{+2}, Mn^{+2}, and Ni^{+2}. The ions are roughly divided into three groups. The group A ions have very insoluble oxides or hydroxides. The group B ions are poorly coordinated by NH_3 and have very insoluble carbonates; magnesium is included in group B even though it is precipitated separately. Group C metal ions are strongly coordinated by NH_3. This prevents their precipitation in the previous steps.

Note that almost all of the solutions can safely go down the sink in moderate amounts. The barium sulfate should be collected, but its storage and disposal should not pose a serious problem in the small amounts used in the tests. The organic compounds used to test for the transition metal ions should be handled with care as they are irritants and suspected carcinogens. Once in solution, they are used in small amounts that should not pose a serious hazard.

Procedure

Separation of Ion Groups: Unknown and Known (with each group)

1. Place 1 mL of your test solution in a medium test tube.

2. Add l2 drops of 6 M HNO_3, 3 mL of 6 M NH_3(aq), and stir. Wait five minutes, then centrifuge and decant. The solid may contain $Al(OH)_3$, $Fe(OH)_3$, and $Mn(OH)_2$. *Save the solid for Group A analysis*. Use the solution in the next step.

3. To the solution from step 2, add 2 mL of 1 M $(NH_4)_2CO_3$ solution and stir. Centrifuge and decant. The solid may contain $BaCO_3$ and $CaCO_3$. *Save the solid for Group B analysis.* Use the solution in the next step.

* Adapted from Petty, John T. A Short Qualitative Analysis Scheme without Hazardous Wastes

4. To the solution from step 3, add 1 mL of 1 M Na_2HPO_4 solution. A white precipitate of $MgHPO_4$ indicates the presence of magnesium ion. Centrifuge and decant. *Save the solution for Group C analysis*.

$$Mg^{+2}(aq) + HPO_4^{-2}(aq) \rightarrow MgHPO_4(s) \quad (1)$$

5. To expedite your time, you should begin Group C step 1 before beginning Group A below as it takes awhile to evaporate the Group C ions to dryness. While waiting for the solution in the evaporating dish as instructed in C-1 to dry, carry out Groups A and B analyses.

Analysis of the Groups of Ions: Group A (Al^{3+}, Fe^{3+}, Mn^{2+})

1. Add 6 M NaOH to solid A from step 2 until pH > 7 (about 1 mL) and stir vigorously with a glass stirring rod. Centrifuge and decant. In strong base, $Al(OH)_3$ solid will dissolve back into the solution, forming the complex ion $Al(OH)_4^-$.

2. To the solution, add 1 M H_3PO_4 dropwise until slightly acidic. A white precipitate indicates aluminum ion.

$$Al(OH)_4^-(aq) + H^+(aq) \rightarrow Al(OH)_3(s) + H_2O(l) \quad (2)$$

3. To the solid from step 1, add 2 mL of H_2O. Then add 6 M HNO_3 dropwise until acidic and stir to dissolve the solid in order to isolate Fe^{+3} and Mn^{+2} ions. To ensure a low pH, once solution is acidic, add 2 MORE mL of HNO_3 and divide the solution into two test tubes.

4. To one test tube, add 2 – 3 drops of 0.5 M KSCN. A dark-red solution indicates iron(III) ion.

$$Fe^{+3}(aq) + SCN^-(aq) \rightarrow FeSCN^{+2}(aq) \quad (3)$$

5. To the other test tube, add a spatula tip of sodium bismuthate ($NaBiO_3$). Mix and wait five minutes. A purple solution indicates manganese(II) ion has oxidized to MnO_4^-. (The color of the solution will fade on standing as it reacts in the air.)

$$2Mn^{+2}(aq) + 14H^+(aq) + 5BiO_3^-(aq) \rightarrow \underset{\text{purple}}{2MnO_4^-(aq)} + 5Bi^{+3}(aq) + 7H_2O \quad (4)$$

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Group B (Ba^{2+}, Ca^{2+})

NOTE: Magnesium ion is technically part of Group B. However, the test for magnesium ion has already been performed in step 4 of the ion group separation.

1. Add 1 mL of water to solid B from step 3 of the ion group separation, and then slowly add 6 M HCl dropwise. Stir until the solid has dissolved.

2. Add 1 mL of l M Na_2SO_4 and stir. A white precipitate indicates barium ion. Centrifuge and decant.

$$Ba^{+2}(aq) + SO_4^{-2}(aq) \rightarrow BaSO_4(s) \quad (5)$$

3. To the solution, add 3 drops of 6 M NH_3(aq) and 1 mL of 0.3 M $(NH_4)_2C_2O_4$ solution. Stir and let stand for 1 min. The formation of a white precipitate indicates calcium ion.

$$Ca^{+2}(aq) + C_2O_4^{-2}(aq) \rightarrow CaC_2O_4(s) \quad (6)$$

Group C (Co^{2+}, Cu^{2+}, Ni^{2+})

1. Pour the solution for Group C analysis containing $Co(NH_3)_6^{+2}$, $Cu(NH_3)_4^{+2}$, and $Ni(NH_3)_6^{+2}$ from step 4 of the ion group separation into an evaporating dish and heat gently over a beaker of boiling water in a fume hood to dryness. *Hint: If the dried residue appears purple, this is an indication of the presence of Co^{2+}. If the residue has a greenish color, this is an indication of the presence of Ni^{2+} while a blue color of the residue is an indication of the presence of Cu^{2+}. You still have to carry out the procedure below to further confirm these "hints."*

2. Dissolve the solid from step 1 in 2 mL of 1 M H_3PO_4. Then add 1 mL of 1 M Na_2HPO_4 and divide it equally into three test tubes.

3. To the first test tube add a spatula tip of KI and stir. A brown solution with a pale tan precipitate indicates copper(II) ion.

$$Cu^{+2}(aq) + 2\,I^{-}(aq) \rightarrow CuI_2(s) \quad (7)$$

4. To the second test tube add Na_2HPO_4 until basic and then add a few drops of 1% dimethylglyoxime solution (DMG^{-}). A red/pink precipitate indicates nickel ion.

$$Ni(NH_3)_6^{+2}(aq) + 3DMG^{-}(aq) \rightarrow Ni(DMG)_3^{-}(aq) + 6NH_3(g) \quad (8)$$

5. To the third test tube, add 2 – 3 drops of 0.5% 1-nitroso-2-naphthol in 95% ethanol solution and stir. A red-brown precipitate indicates cobalt(II) ion.

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Pre-Lab Assignment: Prepare a complete flow diagram for the separation and identification of the various cations presented in this experiment.

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Experiment Results:

UNKNOWN______ IONS PRESENT________________________

Post-Lab Questions:

1. The precipitates of iron(III) ion and manganese(II) ion are hydroxides. What is the purpose of adding 6 M $HNO_3(aq)$ in step 3 of the Group A analysis?

2. In step 2 of Group B, Na_2SO_4 is added. A white precipitate indicates the presence of barium ion. Look up and write down the appropriate K_{sp} values and suggest a reason why a calcium precipitate does not form along with the barium precipitate.

3. Describe any modifications (if any) that you discovered that worked for your analysis. How would you improve this experiment?