Experiment 14 - Qualitative Analysis

Introduction

Qualitative analysis involves the identification of the substances in a mixture. When chemical methods are used in the identification of mixtures of metal cations, these ions are usually separated before identification can occur. After they have been separated, identification of each cation depends on the observation of a characteristic chemical reaction. Solubility equilibrium and complex-ion equilibrium play crucial roles in the separations and subsequent identifications.

Purpose

You will learn to separate and identify each cation in a mixture of Ag^+, Cu^{2+}, Zn^{2+}, and Ca^{2+} ions. You will also receive an unknown mixture for qualitative analysis. This mixture can contain any or all of these cations.

Concept of the experiment

You will be working with mixtures of Ag^+, Cu^{2+}, Zn^{2+}, and Ca^{2+} ions. These cations belong to Analytical Groups I, II, III, and IV. Time does not permit us to include a cation from Analytical Group V. The intention of this experiment is to give you a better appreciation of this separation scheme through a few examples. Before you try to do the experiment, spend some time studying the scheme and reading the following description.

Hydrochloric acid will be used to precipitate Ag^+ as white AgCl. If you do not observe a precipitate with your unknown mixture, this cation cannot be present. The formation of a precipitate, however, is not considered sufficient evidence for the presence of Ag^+ in either a known or an unknown mixture. As a confirmatory test for this cation, this precipitate should dissolve in aqueous ammonia with the formation of a complex ion and should reappear when the solution is treated with an acid.

Hydrogen sulfide is required for the next two separations. A saturated solution (0.10 *M)* of this substance will be generated by heating a solution of thioacetamide, CH_3CSNH_2. Hydrolysis (reaction with water) has the following result:

$$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S$$

This reagent will be used to precipitate Cu^{2+} as black CuS from a 0.3 *M* H_3O^+ solution and to precipitate Zn^{2+} as white ZnS from a weakly basic solution. Another problem will show that both CuS and ZnS will precipitate from a weakly basic solution but that only CuS will precipitate from a 0.3 *M* H_3O^+ solution. Therefore, separation of these ions will occur only if precipitation is achieved first under acidic conditions and then under basic conditions. If a precipitate does not form in the acidic solution of your unknown mixture, Cu^{2+} must be absent. Similarly, Zn^{2+} cannot be in your unknown mixture if a precipitate is not formed in the weakly basic solution.

You will then dissolve each of these metal sulfides in nitric acid. This reagent will

oxidize the sulfide ion to elemental sulfur. The solution should be blue for $Cu^{2+}_{(aq)}$ and colorless for $Zn^{2+}_{(aq)}$. The confirmatory test for each cation involves the addition of potassium ferrocyanide, $K_4Fe(CN)_6$, to these solutions. A red-maroon precipitate confirms the presence of Cu^{2+}, whereas a white precipitate confirms the presence of Zn^{2+}. You should note that $Fe(CN)_6^{4-}$ is a complex ion that is considerably less toxic and dangerous than the cyanide ion, CN^-.

Finally Ca^{2+} will be precipitated as white $CaCO_3$ by the addition of $(NH_4)_2CO_3$. This precipitate will dissolve in an acid with the evolution of carbon dioxide. If a precipitate does not form, Ca^{2+} cannot be present in your unknown mixture. The confirmatory test for this cation involves the precipitation of the white oxalate, CaC_2O_4, upon the addition of $K_2C_2O_4$.

Procedure

Getting started

1. Obtain 6 small test tubes.
2. Set up a boiling water bath using a beaker of water, a ring stand, an iron ring, wire gauze, and a laboratory burner. Place the bath in a hood if one is available. If not, use an inverted conical filter funnel connected by rubber tubing to a water aspirator. Clamp the funnel so that it will be positioned directly over the test tube in which hydrogen sulfide will be generated (Step 10 of the analysis).
3. Obtain your unknown mixture and record its identification number and color. Does the color provide a clue about the presence or absence of one of the possible components in the mixture?
4. Obtain 1 mL of the known mixture. This solution contains $AgNO_3$ (0.1 *M),* $Cu(NO_3)_2$ (0.2 *M),* $Zn(NO_3)_2$ (0.2 *M),* and $Ca(NO_3)_2$ (0.2 *M).*
5. Conduct the analysis of the known and unknown solutions simultaneously so that you can compare the results.
6. Use labeled test tubes throughout the experiment so that you do not confuse the known and unknown solutions and precipitates at any time.
7. Obtain instructions for using the centrifuges in the laboratory.

   CAUTION: When you use a centrifuge, do not attempt to stop the centrifuge rotor with your finger or anything else.
8. Obtain instructions for discarding the solutions that you will use in this experiment.
9. Take care in handling the solutions used in this experiment.

   CAUTION: Hydrochloric acid, ammonia, nitric acid, and acetic acid can cause chemical burns in addition to ruining your clothes. If you spill any of these solutions on you, wash the contaminated area thoroughly with tap water and report the incident to your instructor. You may require further treatment.

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Doing the analysis

1. Take 1 mL of the known mixture and 1 mL of the unknown mixture in separate small test tubes.
2. Each of the subsequent additions and operations should be conducted on both the known and the unknown mixtures unless the instructions indicate otherwise.
3. Add 2 drops of 6 *M* HC1. If no precipitate forms, proceed with Step 7. If a precipitate forms, stir the mixture with a clean stirring rod. Centrifuge the mixture for about 1 min.
4. Check for complete precipitation by adding 1 more drop of 6 *M* HC1. Avoid using excess HC1. If a precipitate has formed, centrifuge the mixture and check again for complete precipitation. Continue this process until no precipitate is formed.
5. Decant (pour off) the solution into a clean test tube. Save this solution for Step 7. Use the precipitate in the following step.
6. Add 10 drops of 6 *M* NH_3 to the precipitate. If necessary, stir the mixture with a clean stirring rod until the precipitate dissolves. Add 6 *M* HNO_3 by drops until a white precipitate appears. These reactions confirm the presence of Ag^+.
7. Add 6 *M* NH_3 by drops to the solution from either Step 3 or Step 5 until a drop of the solution on a clean stirring rod causes pink litmus paper to turn blue.
8. Estimate the volume of the solution to the nearest 0.5 mL. Make the estimate by comparing the volume with measured amounts in a similar test tube. Mentally, add 0.6 mL to that volume to account for the dilution that will occur in Step 9. Round the result to the nearest milliliter. Add 1 drop of 6 *M* HC1 to the solution for every milliliter that results from this procedure. The concentration of H_3O^+ in the solution will be 0.3 *M* after the dilution in Step 9 is completed.
9. Add 12 drops of 1 *M* thioacetamide to the solution.

   CAUTION: Thioacetamide is a carcinogen. Avoid contact with your skin.
10. Place the test tube in the boiling water bath for about 10 min. If no precipitate forms during this time, proceed with Step 16. If a black precipitate forms, proceed with the following step.

    CAUTION: In addition to having a foul odor, the hydrogen sulfide generated during the hydrolysis of thioacetamide is extremely toxic. Although only small amounts of H2S usually escape from the solution, work under a hood if possible. If not, use the inverted conical filter funnel and water aspirator described earlier to suck away the escaping H_2S.
11. Centrifuge the mixture and decant the clear solution into a clean test tube. Save the precipitate for Step 12. Test the solution for complete precipitation by adding 3 more drops of 1*M* thioacetamide and reheating for 5 min. If no precipitate forms, save the solution for Step 16. If a precipitate forms, centrifuge the mixture, save the solution for Step 16, and discard the precipitate.
12. Wash the precipitate by stirring it vigorously with 1 mL of distilled water. Use a clean stirring rod. Centrifuge the mixture, save the precipitate, and discard the water.

13. Add 20 drops of 6 *M* $HN0_3$ to the precipitate. Place the test tube in the boiling water bath for several minutes. Stir occasionally with a clean stirring rod. Separate any sulfur or traces of undissolved sulfides by centrifuging. Discard the residue and use the solution in the next step.
14. Add drops of 6 *M* NH_3 carefully until the solution turns pink litmus paper blue. Then add drops of 6 *M* acetic acid until the solution turns blue litmus paper pink.
15. Add 10 drops of 0.1 *M* $K_4Fe(CN)_6$ and mix thoroughly. A red-maroon precipitate confirms the presence of Cu^{2+}.
16. Estimate the volume of the solution from either Step 10 or Step 11 by comparing it with 3 mL of water in a similar test tube. If the volume is 3 mL or less, proceed to the next step. If it is greater than 3 mL, place the solution in the boiling water bath until that volume is attained.
17. Add 10 drops of 6 *M* HC1 followed by 10 drops of 6 *M* NH_3. Then add drops of 6 *M* NH_3 until the solution is basic to litmus paper. Add 5 more drops of this reagent.
18. Add 12 drops of 1*M* thioacetamide. Stir thoroughly and heat for 10 min in the boiling water bath. If no precipitate forms, proceed with Step 23. If a precipitate forms, proceed with the following step.
19. Centrifuge the mixture and decant the clear solution into a clean test tube. Save this solution for Step 23. Use the precipitate in the next step.
20. Wash the precipitate by stirring it vigorously with 2 mL of distilled water to which you have added 1 drop of 6 *M* NH_3. Use a clean stirring rod. Centrifuge the mixture, save the precipitate, and discard the water.
21. Repeat Steps 13 and 14.
22. Add 10 drops of 0.1 *M* $K_4Fe(CN)_6$ and mix thoroughly. A white precipitate confirms the presence of Zn^{2+}.
23. Add 10 drops of 3 *M* $(NH_4)_2CO_3$ to the solution from either Step 18 or Step 19. If no precipitate forms, you have completed the analysis. If a white precipitate forms, proceed with the next step.
24. Centrifuge the mixture, save the precipitate, and discard the solution.
25. Wash the precipitate in the same manner as in Step 12.
26. Dissolve the precipitate by adding 5 drops of 6 *M* acetic acid.
27. Make the solution basic to litmus paper using 6 *M* NH_3.
28. Add 10 drops of 1 *M* $K_2C_2O_4$. A white precipitate that should form within a few minutes confirms the presence of Ca^{2+}.

    CAUTION: Wash your hands thoroughly. Oxalate solutions are poisonous.
29. Record the cations that are present in the unknown mixture.

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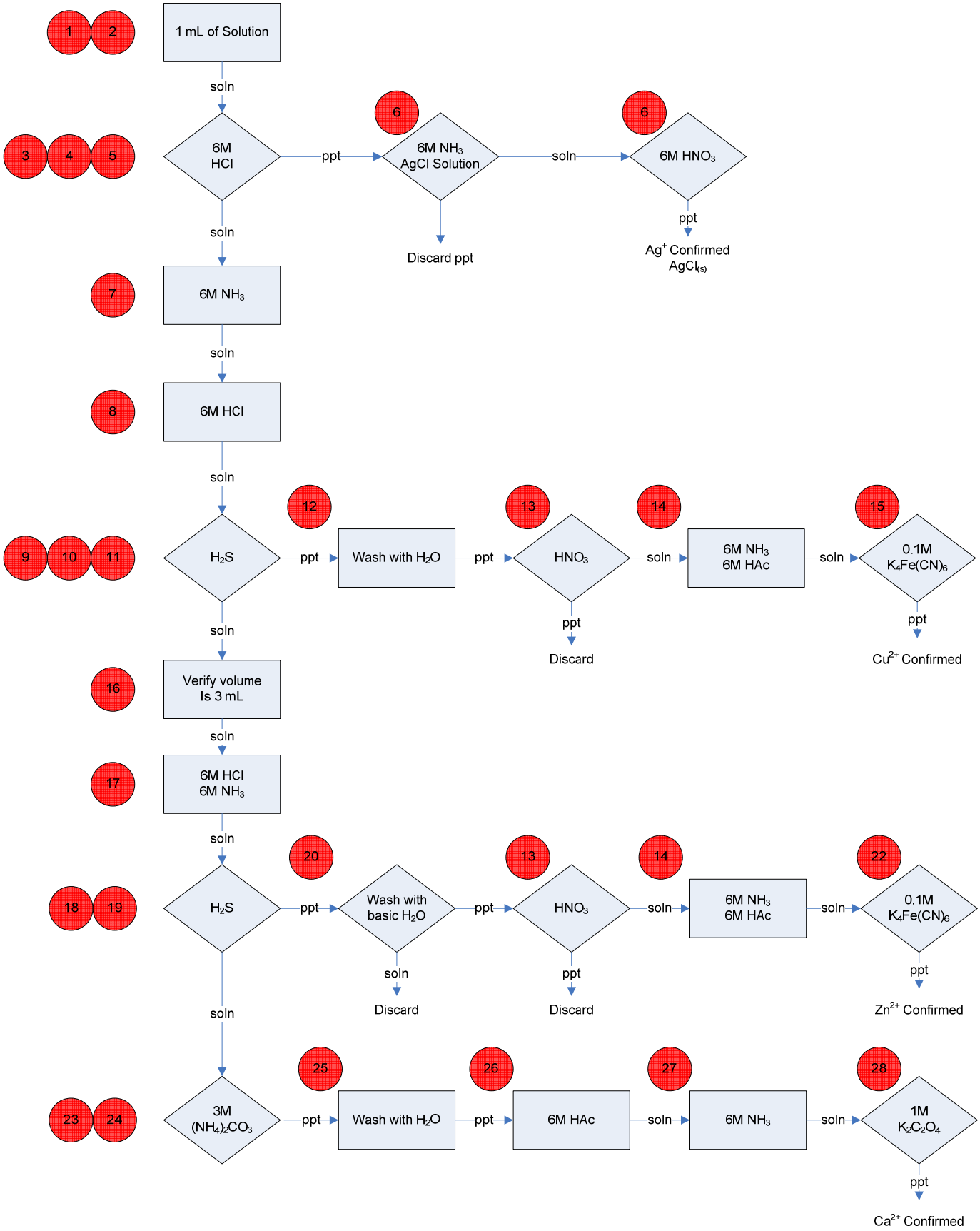

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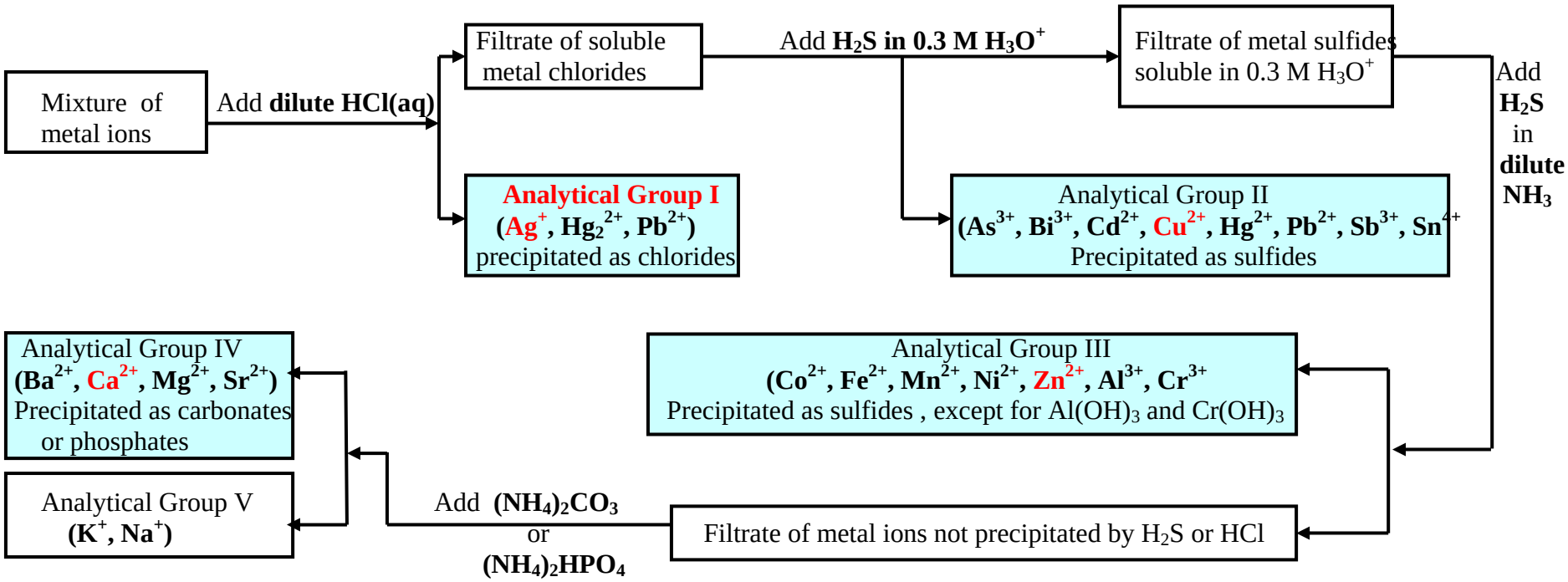

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