Experiment 9

Who's Guilty?

Pre-Lab Assignment

Before coming to lab:

- Read the lab thoroughly.
- Answer the pre-lab questions that appear at the end of this lab exercise. The questions should be answered on a separate (new) page of your lab notebook. Be sure to show all work, round answers, and include units on all answers.
- Follow the guidelines in the "Lab Notebook Policy and Format for Lab Reports" section of the lab manual to complete in your lab notebook the following sections of the report for this lab exercise: Title, Lab Purpose, Procedure and Data Tables.

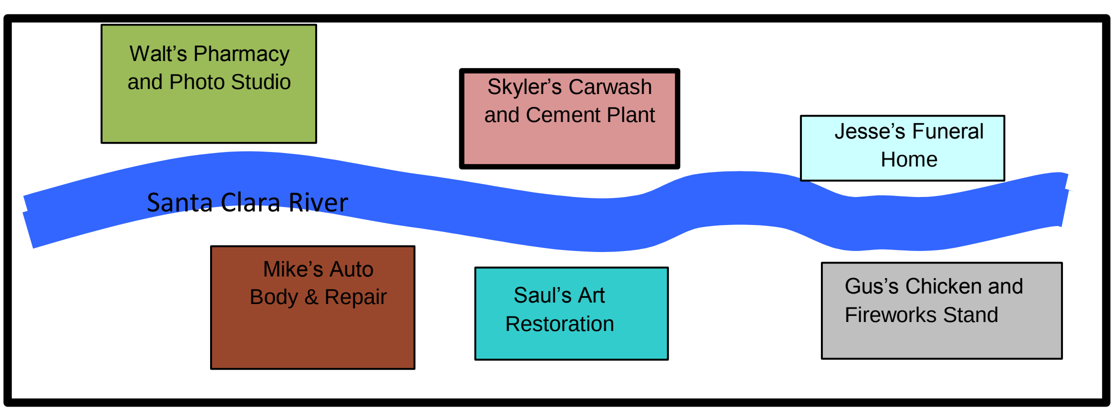
Purpose

In this experiment, you will develop a scheme for separating and identifying a selected group of cations in an unknown sample. You will then apply your scheme to determine the source of "pollution" in a sample.

Background

The City of Ventura is trying to identify the source of metal contamination detected in the Santa Clara River. Excessively high levels of metal cations have been detected but not yet identified. Possible cations are Ag^{+}, Ni^{2+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, and Ba^{2+}. The businesses that are likely suspects for contributing one or more metal cations to the river water (Figure 1) are: Walter's High Margin Pharmacy and Photo Studio (**1**), Skyler's Carwash and Cement Plant (**2**), Jesse's Funeral Home (**3**), Mike's Auto Body & Repair (**4**), Saul's Art Restoration (**5**), and Gus's Chicken and Fireworks Stand (**6**). These suspects all use different cations in their businesses. Silver solutions are used in photograph processing. Cement plants are sources of chromium. Funeral homes use iron in the embalming process. Automobiles contain nickel solutions. Zinc is used as a white pigment in art, and barium is used in fireworks.

You will develop a qualitative analysis scheme to separate each cation and thereby determine the identity and source of the pollution. For the separation and detection of the cations in question, you will use reactions that involve different tendencies of these ions to precipitate, form ammonia complex ions, or form soluble hydroxide complexes.



Predicting reaction products

In addition to developing a separation scheme, you will need to complete and balance the equations for each of the reactions occurring during the experiment as part of your post-lab. The reactants are given in each case. With the exception of one reaction which is an oxidation-reduction reaction, all the reactions in this experiment are of three types:

1. formation of an insoluble salt (precipitation reaction)
2. formation of soluble hydroxide complex ions
3. formation of amine complex ions

Formation of an Insoluble Salt (Precipitation Reaction)

To predict the formula of an insoluble precipitate, use the **cation** under study and the **anion** from the reagent added. For example, if you mix Pb^{2+} solution with 3.0 M HCl, you observe a white precipitate. The net-ionic equation is

$$Pb^{2+} + 2\ Cl^- \rightarrow PbCl_{2(s)}$$

Recall that NaOH or NH_3 are both bases (sources of OH^-). When they are added to a solution and a precipitate forms, it will be a metal hydroxide.

Formation of Hydroxide Complex Ions

Hydroxides such as $Zn(OH)_2$ and $Al(OH)_3$, may dissolve in a strong base. You will test for this behavior by first adding just enough NaOH to make a solution basic. This will cause most metal cations to precipitate as metal hydroxides. You will then add excess NaOH to see if the metal hydroxide dissolves. For example, if you add 1 drop of NaOH to Pb^{2+} solution, you see a white precipitate which dissolves when an excess of 8- 10 drops of NaOH is added.

The net-ionic equations are:

(OH^- added to just basic) $\quad Pb^{2+} + 2OH^- \rightarrow Pb(OH)_{2(s)}$

(more OH^- added - in excess) $\quad Pb(OH)_{2(s)} + 2OH^- \rightarrow Pb(OH)_4^{2-}$

The ion $Pb(OH)_4^{2-}$ is called a complex ion. In this experiment, any soluble complexes that form will involve the metal cation joined together with four OH^- as in the previous example. Remember to use this information when balancing your reactions.

Formation of Ammine Complex Ions

You will test for the formation of amine complex ions by first adding just enough NH_3 solution to make the cation solution basic (in which case most metal hydroxides precipitate as described above), then by adding excess NH_3 to see if the metal hydroxide dissolves. For example, if you added 1 drop of NH_3 solution to a Cd^{2+} solution, you would see a white precipitate which dissolves after adding 8-10 drops excess NH_3. The net-ionic equations are:

(NH_3 added till basic) $\quad Cd^{2+} + 2NH_3 + 2H_2O \rightarrow Cd(OH)_{2(s)} + 2NH_4^+$

(more NH_3 added- in excess) $\quad Cd(OH)_{2(s)} + 4NH_3 \rightarrow Cd(NH_3)_4^{2+} + 2OH^-$

The ion $Cd(NH_3)_4^{2+}$ is an ammine complex. Many transition metal cations form ammine complexes, as well as complex ions with other groups besides NH_3 or OH^- (called ligands). The number of ligands attached to a metal is called the **coordination number**. The cations in this study have the following coordination numbers when they form complex ions. Ag^+(2), Ni^{2+}(6), Fe^{3+}(6), Cr^{3+}(4), Zn^{2+}(4). Use these coordination numbers to determine the number of NH_3 groups bonded to the metal for any of the cations you observe forming ammine complexes when balancing your reactions. This will be especially important when balancing your reactions. You will learn more about coordination compounds in chapter 23 of your book.

Dissolving a Precipitate by Adding a Strong Acid

Frequently in qualitative analysis, we need to bring a precipitate back into solution. There are many different ways to dissolve a precipitate. Most of these involve chemical reactions which compete with precipitate formation. Common methods involve forming a complex ion with the cation (as in the above examples) or adding H^+ if the insoluble salt contains the anion of a weak acid. An example of this is:

$$NiS_{(s)} + 2\ H^+ \rightarrow Ni^{2+} + H_2S$$

Redox Reactions

The only oxidation-reduction reaction you will observe is that of $Cr(OH)_4^-$ with H_2O_2 in basic solution. The products are CrO_4^{2-} from the $Cr(OH)_4^-$ and OH^- from the H_2O_2. Using this information, you can balance the redox equation.

Development of Separation Scheme

On day 1 of the lab, you will be testing known solutions of each individual cation and recording your results. Using these observations, before your lab meets for day two of the lab you must develop a scheme in flow chart form for separating and identifying the presence or absence of all six cations in an unknown. **You must get your flow chart approved by your instructor before lab starts.** You will not be issued an unknown until your flow chart is approved.

The better prepared you are before lab the more success you will have when using your scheme on the "river water" samples! An incomplete scheme will eat up your valuable time and lead you to incorrect or unsubstantiated conclusions. *To be fair to all investigators no one will be allowed to work past the end of the lab period.*

To develop your scheme for separating the ions in the unknown, use the reagents and results from steps 1-4 below. Ideally, you would add a reagent that will precipitate out only one cation which can then be separated by centrifugation. That isn't entirely possible with these reagents. You will at some point have to separate the group of ions into two smaller groups with some cations in the precipitate you form and others left in solution. These mixtures can then be further treated to completely separate the cations.

Once you have separated one cation away from the others, you need to run a confirmatory test to prove its presence using the tests in steps (5)-(10) below.

An example qualitative analysis scheme for a different set of cations and test reagents than the ones you'll use is shown later in this lab handout.

Note: You can add 6.0 M HNO_3 dropwise to neutralize excess base. To dissolve metal hydroxide precipitates, add 10 drops of water, then 6.0 M HNO_3 with stirring until dissolved.

General Technique Reminders

Mixing of reagents: A dropper should be used to add small quantities of one reagent to another. For qualitative analysis, the general rule of thumb is that 1 mL = 20 drops, using a standard size dropper. When mixing two or more reagents, always stir the mixture before drawing any conclusions about the reaction.

Heating of solutions in test tubes: The safest, simplest way to heat a small amount of solution in a small test tube is in a boiling water bath. For the small (4") test tubes, use a 250 mL beaker containing 1 ½ inches boiling water. Put the test tube in the boiling water for about 5 minutes, and stir a couple of times during the 5 minutes.

Testing acidity or basicity: To test a solution for acidity or basicity, stir it with a stirring rod and touch the wet rod to a piece of litmus paper. Litmus is red in acidic and blue in basic solutions. Never immerse the litmus paper in the solution in the test tube.

Procedure

Safety

Most of the acids and bases used are very concentrated and can cause chemical burns if spilled. Handle them with care. Wash acid or base spills off of yourself with lots of water. Small spills (a few drops) can be cleaned up with paper towels. Larger acid spills can be neutralized with baking soda, $NaHCO_3$, and then safely cleaned up. Neutralize base spills with a vinegar solution (dilute acetic acid). Solutions containing silver ions cause stains that do not appear immediately. If you suspect that you spilled any of these solutions on yourself, wash them off with soap and water.

Wash your hands when finished.

Wear goggles and an apron.

Waste Disposal

Your teacher will provide a waste container for the solutions used in this experiment.

Preliminary Tests

You will study the reactions of the six cations Ag^+, Ni^{2+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, and Ba^{2+} with various reagents. Record all observations such as initial colors, precipitate formations, color changes, etc. A sample Data Table is provided later in this lab handout. It will be used to develop a scheme for separating these cations. Copy this table into your lab notebook.

Perform all tests in your small test tubes.

1. **Reaction with dilute HCl.**

To 10 drops of each cation solution, add 1 mL (20 drops) of 3.0 M HCl. Record your observations for each sample. Any precipitates formed are metal chlorides.

2. **Reaction with $NH_3 + H_2O$**.

a. To 10 drops of each cation solution, add 1 drop of 1.0 M NH_3 solution and mix. Test each solution for basicity. To any mixture which is not basic, add additional 1.0M NH_3 dropwise until just basic. Any precipitates formed are metal hydroxides.

b. To the above basic mixtures, add 10 drops of concentrated 15.0M NH_3. Note any color changes or precipitates that dissolve to detect the formation of amine complex ions.

3. **Reaction with NaOH and oxidation with H_2O_2**

a. To 10 drops of each cation solution, add 1 drop of 3.0 M NaOH and mix. Test each solution for acidity. To any mixture which is not basic, add additional 6.0 M NaOH dropwise until just basic. Any precipitates formed are metal hydroxides.

b. To the above mixtures, add 20 drops of 3.0 M NaOH and mix. Note any color changes and any precipitates that dissolve to detect the formation of any hydroxide complex ions.

c. To the above test tubes, add 10 drops of 3% H_2O_2 and heat for 5 minutes in a boiling water bath. Stir a couple of times while heating. Note any changes which occur.

4. **Reaction with H_2SO_4**

a. To 10 drops of each cation solution, add 5 drops of 3.0 M H_2SO_4 and mix. Any precipitates that form are metal sulfates.

Confirmatory Tests

Again, perform these tests in a small test tube.

5. **Ag^+ test**

The formation of white AgCl on addition of HCl as in saw in step (1) above is sufficient to confirm Ag^+. It is not necessary to repeat this test.

6. **Fe^{3+} test**

To an Fe^{3+} solution (10 drops), add 5 drops of 0.2 M KSCN. This will form the complex ion $Fe(SCN)_6^{3-}$,a deep red complex ion.

7. **Cr^{3+} test**

To a CrO_4^{2-} solution (10 drops), add 6.0 M $HC_2H_3O_2$ until acidic; then add 2- 3 drops of 0.1 M $Pb(C_2H_3O_2)_2$ solution. A yellow precipitate of $PbCrO_4$ will form.

8. **Ni^{2+} test**

Take 10 drops of Ni^{2+} solution; make it just basic with 6.0 M NH_3. To this mixture, add 10 drops of dimethylglyoxime. The formation of red precipitate confirms Ni^{2+}.

9. **Zn^{2+} test**

To 10 drops of Zn^{2+} solution, add 6.0 M HNO_3 until just acidic; then add 10 drops of $K_4Fe(CN)_6$. Formation of a pale yellow precipitate of $K_2ZnFe(CN)_6$ confirms Zn^{2+}.

10. **Ba^{2+} test**

The formation of white $BaSO_4$ precipitate, noted in step (4) above on addition of 3.0 M H_2SO_4, is sufficient to confirm Ba^{2+}. It is not necessary to repeat this step.

Data Tables

Below is a sample data table for the Preliminary Tests

Reagents	Ag^{+}	Fe^{3+}	Cr^{3+}	Ni^{2+}	Zn^{2+}	Ba^{2+}..
Test 1 3 M HCl						
Test 2 1 M NH_3 until basic						
15 M NH_3 in excess						
Test 3 3 M NaOH until basic						
3 M NaOH in excess						
3 M NaOH in excess, H_2O_2 and heat						
Test 4 3 M H_2SO_4						

Observations for the confirmatory tests

5. Ag^{+} test:
6. Fe^{3+} test:
7. Cr^{3+} test:
8. Ni^{2+} test:
9. Zn^{2+} test:
10. Ba^{2+} test

3. Before the second day of this lab, construct a flow chart and get it approved by your instructor.

- This scheme should take advantage of the solubility differences among the salts, hydroxides, and complexes, the redox properties of the metal cations, and include all the confirmatory tests.

- Your task is to design a qualitative analysis scheme of separation and identification that is effective, that entails the fewest steps, and that achieves the cleanest separations.

- Your qualitative analysis scheme should be presented as a top down design (as shown in the example on pg 167 of this lab handout).

- A confirmation test can only be used to confirm a cation is present/absent. It cannot be used to separate a cation from the other cations.

4. After you are done with your unknown analysis, indicate which cations are in your sample and what businesses are guilty of polluting the Santa Clara River.

Post-Lab Questions

Complete and balance the following equations for the preliminary tests you formed in net-ionic form. Be sure to indicate the phase**.** In addition, write the step number that the reaction belong with next to each balanced reaction.

Step Number from your scheme

1. $Ag^{+} + Cl^{-} \rightarrow$

2. $Ag^{+} + NH_3 + H_2O$ (until basic) $\rightarrow$

3. $AgOH_{(s)} + NH_3$ (excess) $\rightarrow$

4. $Ag^{+} + NH_3$ (excess) $\rightarrow$

5. $Ag^{+} + OH^{-} \rightarrow$

6. $Fe^{3+} + NH_3 + H_2O \rightarrow$

7. $Fe^{3+} + OH^{-} \rightarrow$

8. $Fe(OH)_{3(s)} + H^{+} \rightarrow$

9. $Fe^{3+} + SCN^{-} \rightarrow$

10. $Cr^{3+} + NH_3 + H_2O \rightarrow$

11. $Cr^{3+} + OH^{-}$ (until basic) $\rightarrow$

12. $Cr(OH)_{3(s)} + OH^{-} \rightarrow$

13. $Cr(OH)_{3(s)} + H^{+} \rightarrow$

14 $Cr(OH)_4^{-} + H_2O_2 + OH^{-} \rightarrow$ (Note: This is a redox equation)

15. $CrO_4^{2-} + Pb^{2+} \rightarrow$

16. $Zn^{2+} + NH_3 + H_2O$ (until basic) $\rightarrow$

17. $Zn(OH)_{(s)} + NH_3$ (excess) $\rightarrow$

18. $Zn^{2+} + NH_3$ (excess) $\rightarrow$

19. $Zn^{2+} + OH^{-}$ (until basic) $\rightarrow$

20. $Zn(OH)_{2(s)} + OH^{-}$ (excess) $\rightarrow$

21. $Zn^{2+} + OH^{-}$ (excess) $\rightarrow$

22. $Zn(OH)_2 + H^{+} \rightarrow$

23 $Zn^{2+} + K^{+} + Fe(CN)_6^{4-} \rightarrow$

24. $Ni^{2+} + NH_3 + H_2O$ (until basic) $\rightarrow$

25. $Ni(OH)_{2(s)} + NH_3$ (excess) $\rightarrow$

26. $Ni^{2+} + NH_3$ (excess) $\rightarrow$

27. $Ni^{2+} + OH^{-} \rightarrow$

28. $Ni(OH)_{2(s)} + H^{+} \rightarrow$

29. $Ba^{2+} + SO_4^{2-} \rightarrow$

A Note on Net Reactions

The balanced net reaction describes the chemical changes of any reaction. It is balanced in the usual sense: as many moles of each element in all the reactants as in all the products, and a net charge for all reactants equal to that for all products. It is a net reaction in the sense that only those species in solution that actually change or participate in new bonding situations are included. For example, in the confirming test for Fe^{3+}, KSCN is added to a solution containing Fe^{3+}. The net reaction, however, does not mention KSCN, since it dissociates in solution to the potassium ion, K^{+}, and the thiocyanate ion, SCN^{-}. Only the thiocyanate ion is involved in the chemistry; the ammonium ion is a spectator ion. Thus, we write the balanced net reaction as

$$Fe^{3+} + 6\ SCN^{-} \rightarrow Fe(SCN)_6^{3-}$$

Writing net reactions thus requires you to be able to identify the reacting species in solution as well as the resultant new product, be it solid precipitate or, as in this case, a complex ion that stays in solution.

Pre- Lab Questions

1. The simplest method of showing a separation scheme is in flow chart form. The table below gives you an example of three cations (Pb^{2+}, Cu^{2+}, and Ba^{2+}) with various reagents. Construct a flow chart from the table for separating these three ions from each other. See page 11 of this lab for an example.

Reagent	**Pb^{2+}**	**Cu^{2+}**	**Ba^{2+}**
HCl	White precipitate	No reaction	No reaction
H_2SO_4	White precipitate	No reaction	White precipitate

2. Many of the reactions in this experiment involve the joining of a cation with a hydroxide to form a soluble complex. How many hydroxide ions will join with the metal cations in this lab?

3. How do you properly test to see if a solution is acidic or basic?

4. What is a coordination number?

5. Complete and balanced the reactions involved in confirmatory steps 5, 6, and 10.

Step 5 $Ag^{+} + Cl^{-} \rightarrow$

Step 6 $Fe^{3+} + SCN^{-} \rightarrow$

Step 10 $Ba^{2+} + SO_4^{2-} \rightarrow$

Sample **Separation Scheme for reference:**