INTRODUCTION TO THE GROUP IV AND V CATIONS

The cations left after separation of the Group III cations are those of Group IV ($\text{Ba}^{2+}$ and $\text{Ca}^{2+}$), and those of Group V ($\text{Mg}^{2+}$, $\text{Na}^+$, $\text{K}^+$ and $\text{NH}_4^+$). The group IV cations: barium and calcium, are commonly precipitated as carbonates from a properly buffered solution. However, in this procedure the barium will be precipitated out first as the insoluble sulfate (calcium sulfate being soluble in an acidic solution), and then after the barium has been separated the calcium will be precipitated as the insoluble oxalate. The group V cations: magnesium, sodium, potassium, ammonium, are soluble and do not precipitate with any of the precipitating agents used in groups I through IV. In group V the magnesium ion will be separated as an insoluble phosphate. Potassium and sodium will be detected using a flame test, and ammonium ion will be identified by the release of ammonia gas when combined with a strong base.

When exposed to a flame, certain elements emit light of a characteristic color. As part of our analysis, flame tests of known samples of the Group IV cations are necessary in order to become familiar with the characteristic color emitted by each one. Individual known sample solutions can be flame tested directly or the cation can be precipitated and a flame test performed on the precipitate. In either case, a wire loop is used to introduce the sample into the flame. The loop of the flame test wire must first be thoroughly cleaned of any trace contamination. Begin by lighting a Bunsen Burner and adjusting the flame so that it burns hot; that is it appears blue, not yellow. Then dip the wire loop in 6 M hydrochloric acid (in a test tube) and insert the loop into the hottest part of a Bunsen Burner flame; the tip of the inner blue cone. If the wire is contaminated, the flame will exhibit a color characteristic of the contaminant. Repeat the process of dipping the wire loop into the hydrochloric acid and then inserting it into the flame until no more contamination is apparent. Note that upon sufficient heating the test wire itself will turn the flame orange. After cleaning the wire, it can be used to test a solution or a precipitate.

To test a solution, dip the wire loop into the solution and then insert it into the flame, observing the color that is emitted. For the known solutions, do not insert the wire loop directly into the reagent bottle. Instead, place a small amount of the solution into a test tube for use. Each metal cation may not emit at the same burner temperature. Therefore, when performing flame tests best results are often obtained by slowly bringing the wire loop containing the sample across the flame from the side. As the wire moves across the flame, it is subjected to a range of temperatures within the flame. This method of bringing the loop slowly across the flame is more important for the unknown samples, where concentrations of the emitting elements tend to be lower than in the known samples.

To test a solid, heat a clean wire and touch it to the crystals. The crystals will adhere to the wire and then the wire can be placed in the flame as described above.
1. **BARIUM ION**.

When the test solution is treated with sulfuric acid, only the barium ion forms an insoluble sulfate.

\[ \text{Ba}^{2+} (aq) + \text{SO}_4^{2-} (aq) \rightarrow \text{BaSO}_4 (s, \text{white}) \]

The presence of a white precipitate confirms the presence of the barium ion. If the precipitate is dissolved in hydrochloric acid, and the resulting solution used in a flame test, barium ions impart a characteristic green flame.

2. **CALCIUM ION**.

The formation of a white precipitate when oxalate ion is added to an ammonical solution confirms the presence of the calcium ion.

\[ \text{Ca}^{2+} (aq) + \text{C}_2\text{O}_4^{2-} (aq) \rightarrow \text{CaC}_2\text{O}_4 (s, \text{white}) \]

If the precipitate is dissolved in hydrochloric acid, and the resulting solution used in a flame test, calcium ions impart a characteristic red-orange flame.

3. **MAGNESIUM ION**.

In the ammonical solution, the magnesium will combine with ammonia and a biphosphate ion to produce the insoluble double salt, magnesium ammonium phosphate, which is slow in forming.

\[ \text{Mg}^{2+} (aq) + \text{NH}_3 (aq) + \text{HPO}_4^{2-} (aq) \rightarrow \text{MgNH}_4\text{PO}_4 (s, \text{white}) \]

The precipitate can be dissolved in hydrochloric acid. When the resulting solution is treated with magnesium reagent, 4-(p-nitrophénylazo)resorcinol, and made basic with sodium hydroxide, a precipitate of magnesium hydroxide forms which adsorbs the magnesium reagent, turning the precipitate blue.

\[ \text{Mg}^{2+} (aq) + \text{C}_{12}\text{H}_9\text{N}_3\text{O}_4 (aq) + 2\text{OH}^{-} (aq) \rightarrow \text{Mg(OH)}_2\text{C}_{12}\text{H}_9\text{N}_3\text{O}_4 (s, \text{blue}) \]

The colored precipitate confirms the presence of magnesium ion.

4. **SODIUM ION**.

A flame test on the original sample easily detects the sodium ion. Sodium imparts a bright yellow flame that will mask all other colors, and confirm the presence of sodium ion. The test is very sensitive to trace amounts of sodium, so contamination can cause false positive tests.
5. **POTASSIUM ION**.

A flame test on the original sample detects the potassium ion. The test is much less sensitive than the sodium flame test, and is best observed by evaporating the sample solution and testing the resulting crystals. In the absence of sodium, a violet flame confirms the presence of potassium ion. If sodium is present, view the potassium flame through cobalt glass which absorbs any sodium emission, allowing the violet potassium flame to be visible. Potassium ions can also be verified by adding sodium hydroxide to the original sample, removing any precipitates that form, and treating the supernatant with tetraphenyl borate.

\[ \text{K}^+ (aq) + (C_6H_5)_4B (aq) \rightarrow \text{K(C}_6\text{H}_5)_4\text{B (s, white)} \]

The formation of a white precipitate confirms the presence of potassium ions.

6. **AMMONIUM ION**.

To test for the ammonium ion, advantage is taken of the following equilibrium.

\[ \text{NH}_4^+ (aq) + \text{OH}^- (aq) \rightleftharpoons \text{NH}_3 (g) + \text{H}_2\text{O (l)} \]

Hydroxide ions are added to an ammonium ion solution, driving the equilibrium to the right. Heating drives off the ammonia gas from the system and its presence is detected using moist litmus paper (its odor is also frequently detected).

**PROCEDURE**

0. Students will work individually for this experiment. Except for the laboratory handout, remove all books, purses, and such items from the laboratory bench top, and placed them in the storage area by the front door. For laboratory experiments you should be wearing closed-toe shoes. Tie back long hair, and do not wear long, dangling jewelry or clothes with loose and baggy sleeves. Open you lab locker. Put on your safety goggles, your lab coat, and gloves.

0. Your instructor will indicate how you will perform the qualitative analysis. You will either (1) use the first lab period (day one) to conduct the analysis on the known sample and then the second lab period (day two) to conduct the analysis on the unknown sample, or (2) use two full lab periods to analyze the known sample and the unknown sample simultaneously. Make sure to paste the unknown code label in your Unknown Data Table in the space provided.

**PART A – PREPARATION OF GROUP IV AND GROUP V CATIONS**

0. Take a centrifuge tube to the stock bottle of sample solution (containing Ba$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, and Na$^+$, K$^+$ and NH$_4^+$), found on the cart. Dispense 2 mL of the sample solution into the centrifuge tube using the pipet pump, and label it with your name and as sample. Observe the solution, and record your observations in the Known Data Table. On day two, or, on day one if you are analyzing the known and unknown samples simultaneously, you will place 2 mL of the unknown solution into a clean centrifuge tube, and label it with your name and as unknown. Observe the solution, and record your observations in the Unknown Data Table.
PART B – TEST FOR BARIUM IONS

1. Add 5 drops of 6 M sulfuric acid, mix with the vortex mixer, and centrifuge. A white precipitate shows the presence of barium ions. Test for complete precipitation by adding 1 drop of the 6 M sulfuric acid to the clear supernatant. If cloudiness is observed or a precipitate forms, add another drop, mix, and centrifuge. Repeat this process until no new precipitate forms upon addition of the 1 drop of 6 M sulfuric acid. Obtain two capillary pipets, one for your known and one for your unknown. Centrifuge, then with a capillary pipet decant the supernatant into a clean glass test tube. Divide this supernatant into two approximately equal portions in clean, centrifuge test tubes, label them, and save them for steps 3 and 5. Use the precipitate for step 2.

2. Obtain a platinum loop from the stockroom. Wash the precipitate from step 1 with 3 mL of water, mix, centrifuge, and discard the washings. Dissolve the solid with 2 drops of 6 M hydrochloric acid. Using the platinum loop, perform the flame test several times on the solution. A fleeting pale green flame is due to barium ions. Compare your observations here with those obtained with a 0.1 M barium nitrate solution (found with the Group IV cations on the qual wall).

PART C – TEST FOR CALCIUM IONS

3. To one of the two approximately equal portions of solution prepared in step 1, test solution with litmus, and if it is acidic, add 6 M ammonia carefully until it is slightly basic. Add 2 drops of 1 M potassium oxalate and mix with the vortex mixer. A white precipitate shows the presence of calcium ions. Continue adding drops of 1 M potassium oxalate, with vortex mixing, until precipitation of calcium oxalate is complete. Centrifuge and discard the supernatant. Save the precipitate for step 4.

4. Wash the precipitate from step 3 with 3 mL of water, mix, centrifuge, and discard the washings. Dissolve the solid in 2 drops of 6 M hydrochloric acid. Perform the flame test several times on the solution. A fleeting orange-red sparkly flame is due to calcium ions. This color appears before the yellow sodium flame and the color lasts only a fraction of a second. Compare your observations here with those obtained with a 0.1 M calcium nitrate solution (found with the Group IV cations on the qual wall).

PART D – TEST FOR MAGNESIUM IONS

5. To the second of the two approximately equal portions of solution prepared in step 1, test the solution with litmus, and if it is acidic, add 6 M ammonia carefully until it is slightly basic. Add 4 additional drops of 6 M ammonia, 4 drops of 1 M sodium biphosphate (Na$_2$HPO$_4$, also called disodium monohydrogen phosphate, but not sodium dihydrogen phosphate, NaH$_2$PO$_4$ – read carefully!) and mix with the vortex mixer. Warm gently in a hot water bath, and let it stand for a minute. A white precipitate is highly indicative of the presence of magnesium ions. The precipitate is sometimes very slow in forming. If a precipitate does not form within one minute, heat in a boiling water bath for 2 minutes, cool, and allow to stand for one minute. Centrifuge and discard the supernatant, saving the precipitate for step 6.

6. Dissolve the precipitate from step 5 in a few drops of 6 M hydrochloric acid. Add 1 mL water and 2-3 drops of magnesium reagent. Mix the solution and then, drop by drop, add 6 M sodium hydroxide until the solution is basic to litmus, and then add 5 more drops. If magnesium ions are present, a medium blue precipitate of magnesium hydroxide with adsorbed magnesium reagent forms. Centrifuge out the precipitate from the almost colorless solutions for better observations of the solid.
PART E – TEST FOR SODIUM IONS

7. Evaporate to dryness 1 mL of the original solution. Dissolve the solid with 2 drops of 6 M hydrochloric acid. Using the platinum loop, perform the flame test several times on the solution. A strong yellow flame which persists for several seconds confirms the presence of sodium ions. Compare the results with a sample of 0.1 M sodium nitrate solution (found with the Group IV cations on the qual wall). The test is very sensitive to trace amounts of sodium, so be aware of contamination and clean the platinum loop well (as described in the introduction).

PART F – TEST FOR POTASSIUM IONS

8. Evaporate to dryness 1 mL of the original solution. Dissolve the solid with 2 drops of 6 M hydrochloric acid. Using the platinum loop, perform the flame test several times on the solution. The potassium flame is violet and lasts only for a moment. The test is much less sensitive than that for sodium. If sodium ions are present, look for the potassium flame through blue cobalt glass which absorbs any sodium emission. Compare the flame to that from a saturated potassium nitrate solution (found with the Group IV cations on the qual wall).

9. To 2 mL of the original solution which has not been treated in any way, add 6 M sodium hydroxide dropwise with mixing until the solution is basic to litmus. Centrifuge and decant the supernatant into a clean, glass test tube. Discard the precipitate. To the supernatant, add 5 drops of 0.005 M sodium tetraphenyl borate reagent and mix. Formation of a precipitate indicates the presence of potassium.

PART G – TEST FOR AMMONIUM IONS

10. Pour 1 mL of the original solution that has not been treated in any way into clean a 50 mL beaker. Moisten a piece of red litmus paper, and with water attach the litmus paper to the convex side (the bottom) of small watch glasses. Add 1 mL 6 M sodium hydroxide to the beaker and cover each beaker with a watchglass so that the litmus paper is exposed to any vapor released from the solution. Do not let the solution come in direct contact with the litmus paper. If ammonia is present, the litmus paper gradually turns blue as it is exposed to ammonia gas. If the litmus paper does not turn blue, gently heat the solutions on a hot plate, but do not boil. The nose is also a good detector of ammonia, but is not always as sensitive as litmus paper.

11. Identify the cations present in your unknown and record them at the top of your Data Table.

12. All excess solutions (including any remaining unknown solution) should be disposed of in the Chem 1B Waste Container in the fume hood. Return the unknown test tube to the front counter.

13. Clean and wipe dry your laboratory work area and all apparatus. When you have completed your lab report have the instructor inspect your working area. Once your working area has been checked your lab report can then be turned in to the instructor.
The following is a flow chart for the separation and identification of the Group IV and V cations.

\[ \text{Ba}^{2+}, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+, \text{NH}_4^+ \]

- [(1) 6 M H\text{SO}_4]
  - [white solid (BaSO\text{4})]
    - [(2) 6 M HCl] Green Flame
      - \text{Ba}^{2+}
    - [(3) 6 M NH\text{3}, 1 M K_2C_2O_4]
    - [white solid (CaC_2O_4)]
      - [(4) 6 M HCl] Orange-Red Flame
        - \text{Ca}^{2+}
  - colorless solution (Ca\text{2+}, Mg\text{2+}, Na\text{+, K\text{+}, NH}_4\text{+})
    - [(5) 6 M NH\text{3}, 1 M Na_3HPO_4]
      - [white solid (MgNH}_4\text{PO}_4)]
        - [(6) 6 M HCl] discard
          - Mg\text{2+}
        - [(6) C_{12}H_{9}N_3O_6, 6 M NaOH]
          - [blue solid (Mg(OH)_2\text{C}_{12}H_9N_3O_6)]
            - Mg\text{2+}
            - discard
    - [(7) 6 M HCl] Yellow Flame
      - Na\text{+}
    - [(8) 6 M HCl] Violet Flame
      - K\text{+}
    - [(9) 6 M NaOH] colorless gas (NH\text{3})
      - NH\text{4+}
    - [(10) 6 M NaOH] colorless solution (K\text{+})
      - [K\text{+}]
      - discard
      - [(9) 0.005 M Na(Ph)_2B]
      - white solid (Ph}_2B) colorless solution
        - K\text{+}
        - discard

KNOWLEDGE DATA TABLE

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QUESTIONS

1. Give the flame test color of each of the following ions:

   (a) $\text{Ba}^{2+}$ ________________________  
   (b) $\text{Ca}^{2+}$ ________________________  
   (c) $\text{Na}^+$ _________________________  
   (d) $\text{K}^+$ _________________________  

2. Why must the sodium test and the ammonium test be performed on the original solution?

   _______________________________________
   _______________________________________

3. A solution contains only these ions: silver, tin (IV), iron (III), and potassium. Prepare a flow chart to show how you would separate and identify the four ions in this solution.
4. A solution contains only these ions: mercury (I), lead (II), copper (II), bismuth (III), nickel (II), zinc, barium, and calcium. Prepare a flow chart to show how you would separate and identify the eight ions in this solution.