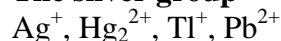


## Qualitative Analysis of Cations

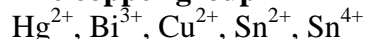
Chemical analysis can be divided into two categories; qualitative analysis – what is present and quantitative analysis – how much is present. In this lab you will learn and apply principles of qualitative analysis for some of the more common metal ions (i.e. those elements that typically form cations in aqueous solution.) This experiment is part of a classical analysis scheme developed by chemists of past generations to identify unknowns. For background references on the qual scheme, you may consult the books by West, *Qualitative analysis and analytic chemical separations*, Hogness, *Qualitative analysis and chemical equilibrium* and Wismer, *Qualitative analysis and ionic equilibrium*. A flow chart is provided to indicate the separation scheme, and a rationale using Hard and Soft Acids and Bases and other principles is given for each separation. The full qualitative analysis scheme for the elements is presented in periodic table format below. In commercial practice the qual-scheme, as it is affectionately known, has largely been surpassed by automated analytic instrumentation. However, the scheme retains real value in teaching many of the chemical attributes of the elements and in the reinforcement of chemical principles. The opportunity to conduct qualitative analyses in the laboratory will teach students new techniques and help to refine those already learned. Most importantly it gives the students some of the sense of discovery in collecting and assimilating the clues to determine the “unknown” composition, as this is such a rewarding part of science.

### Group 1 The silver group



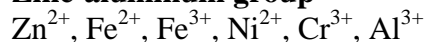
These ions precipitate (as the chlorides) from 0.3M HCl solution. Rationale: *Softest acids react strongly enough with a borderline base to precipitate in acid solution.*

### Group 2 The copper group



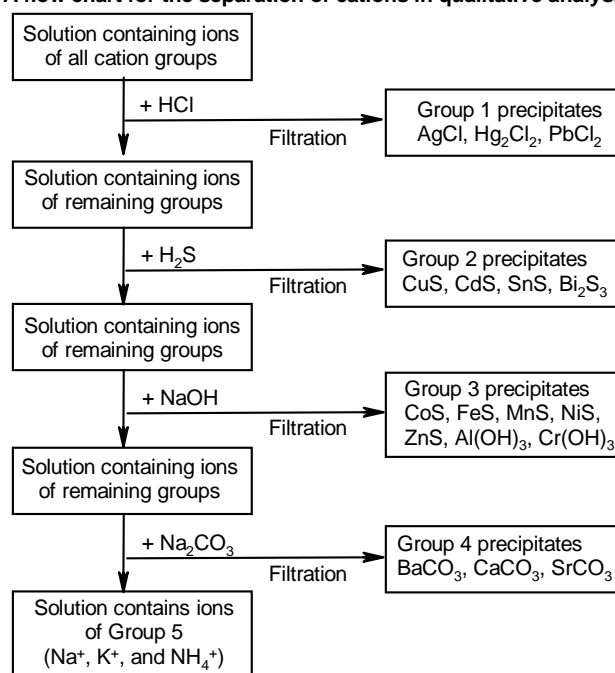
These ions precipitate as the sulfides from 0.3M HCl containing  $\text{H}_2\text{S}$ . Rationale: *Soft acids react with a very soft base.*

### Group 3 Zinc-aluminum group



These ions precipitate from an alkaline solution of  $\text{H}_2\text{S}$ . Some tend to form sulfides, some the hydroxides. Further discrimination is possible, because  $\text{FeS}$ ,  $\text{Cr}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  will redissolve if the precipitate is layered with  $10^{-2}\text{M}$  acid, but  $\text{NiS}$  and  $\text{ZnS}$  will not.

A flow chart for the separation of cations in qualitative analysis

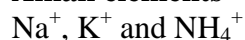


Rationale (1): *ZnS, NiS, FeS as sulfides, i.e. borderline acids bind to a very soft base, when the pH is adjusted so as to weaken the  $\text{M}(\text{OH}_2)_n^{m+}$  hydrated cation.*

Rationale (2):  *$\text{Fe}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$  precipitate because these are hard acids reacting with the hard base  $\text{OH}^-$ . As acidic cations, they will tend to precipitate when the pH is equal to the  $\text{pK}_a$ . These are all hard cations, and therefore prefer the hard base  $\text{OH}^-$ .*

**Group 4 Alkaline earths**

Precipitate from basic solution on the addition of  $\text{CO}_3^{2-}$  in the form of sodium carbonate. The carbonates are the insoluble products formed. Rationale: *These are weakly acidic (Brønsted definition) cations. The carbonates are insoluble because of the favorable lattice energy when the weakly basic carbonate ion reacts with these cations, since the cation and anion are both doubly charged and similar in size.*

**Group 5 Alkali elements**

These have soluble hydroxides and carbonates. They do not precipitate from the qualitative analysis scheme. Rationale: *Lattice energy for carbonates is unfavorable, since the cations are small, and bear a 1+ charge. The hydroxides are soluble because the cations are non-basic, while hydroxide is strongly basic.*

**Qualitative Analysis Scheme for the Cations**

H													Non-metals					
Li	Be												B	C	N	O	F	
Na	Mg	Group 3											Al	Si	P	S	Cl	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu <sub>d</sub>	Zn	Ga	Ge	As	Se	Br		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I		
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po			
Fr	Ra	Ac-Lr	Group 2															
G R O U P 5	G R O U P 4	Group 3																
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

## ***Principles of Qualitative Analysis***

1. Confirmatory Tests: These are tests that determine conclusively that a certain ion is present. Interfering ions are removed before a confirmatory test is done.
2. Separations: These are procedures that separate groups of ions from other groups, or individual ions in a mixture of ions. Separations are followed by confirmatory tests to identify the separated ion.

## ***Techniques of Qualitative Analysis***

1. Be sure to label all tubes and solutions because these accumulate rapidly, and it is very easy to get tubes and/or solutions mixed up.
2. Keep a detailed record of your work in your lab notebook. Leave a page for each test and be sure to include observations, equations, conclusions, etc.
3. Keep a supply of distilled water at your work space. Use it to wash precipitates and for rinsing.
4. Have a waste beaker at your space. You can dump all solutions, washes, etc into your waste beaker and then discard its contents in the heavy metal waste container at the end of the period. This will save time running back and forth.
5. Qualitative analysis is not precise therefore reagents don't have to be measured exactly. Liquid reagents are usually measured in drops. Twenty drops from a medicine dropper is approximately 1 mL. You can calibrate a test tube by adding 1 mL water and marking the level as 1 mL and then adding a second mL, etc and marking that until you have the test tube graduated. Use this test tube as a reference tube when measuring solutions in test tubes by holding it next to the tube you are measuring into.
6. Be sure to mix your solutions well as poorly mixed solutions may lead to false negatives. To mix small volumes, flick the test tube with your forefinger to get a swirling action going in the solution. For large volumes, put a cork into the top of the test tube and mix the solution by inversion. Mixing with a glass stirring rod is also acceptable.
7. When checking the pH of a solution, it must be well mixed otherwise there will be a differential pH gradient in the solution. To check the pH, stick a glass stirring rod into the solution and draw it out. Dab a drop onto a piece of Litmus paper on a glass watchglass. Do not put the litmus paper on the benchtop as there may be residual chemicals on the bench that will interfere.

When checking the pH of solutions containing a precipitate, look at the Litmus response on the liquid portion that has wicked away from the solid, otherwise the solid may mask the response or make it difficult to see.

8. Centrifuging solutions that contain a solid and a liquid is a substitute for filtering the solid to separate it from the liquid portion. When centrifuging, it is critical that the

centrifuge be balanced so the tubes will not break. To do this, place a test tube in one slot and another tube with the same volume of liquid (usually water, multiple samples or another person's sample) diametrically opposite the slot. Coarse precipitates may require only a few seconds of centrifugation while finely divided precipitates may take a few or many minutes. It would be wise to mark your tube before centrifuging in case another person's sample is the same.

The solid remaining in the bottom, after centrifugation, is the precipitate and the solution above the solid is the supernatant or the centrifugate. In this lab we will call it the supernatant. To remove the supernatant from the solid, it can simply be poured off if the solid is very compacted. If the supernatant is required for further tests then it should be removed to a new (labeled) tube otherwise it can be discarded into the waste beaker.

**Note:** It is better to save solutions until you are positive they are not needed.

If the precipitate is only loosely compacted at the bottom of the test tube, then use a Pasteur pipette to draw off the majority of the liquid portion.

9. Decanting a solution is a technique of separating a solid from a liquid. Think about a mixture of sand and water. To separate the sand from the water, you would allow the sand to settle to the bottom of the container and then carefully (so as not to disturb the settled sand) you would pour off the liquid and leave the sand behind. Decanting a liquid from a precipitate is done in the same manner.
10. Precipitation is most often done to remove select ions. It is desirable therefore to make sure that all ions are removed from the solution or that precipitation is complete. To test for *completeness of precipitation*, simply add a drop or two of the precipitating reagent to the clear supernatant (after centrifugation and separation of the liquid from the solid). If more precipitate forms then there are still ions in solution. Centrifuge and combine the precipitates and test the supernatant for completeness of precipitation until no more precipitate forms.
11. Often when an ion precipitates out of solution, it may carry other contaminating ions with it. It is important that precipitates be washed free of any contaminating ions as these may interfere with subsequent testing. To do this, add 0.5 to 1 mL of distilled water to the precipitate. Suspend the precipitate by vigorous shaking or stirring with a stirring rod to wash it, centrifuge and decant the liquid from the solid. The instructions should tell you whether washing is required and how much.
12. Solutions in small test tubes need to be heated in a hot (not boiling) water bath. This allows for even, gentle heating and it is also a safer way to heat solutions in test tubes. To do this place the tube in a hot water bath, without a cork in the top, and with the mouth pointing away from you (towards the back of the hood). Allow the tube to heat for five minutes to ensure complete and even heating. The presence of a precipitate means the solution must be mixed intermittently to prevent the solid from settling and bumping out.

13. When the volume of a solution needs to be concentrated, or reduced, then evaporation is required. Transfer the liquid to a small beaker or an evaporating dish on a hot plate. Using a pair of tongs to hold the container, gently move the container back and forth to mix the liquid and prevent it from burning. Remove it from the heat when the desired volume has been obtained or when there are still a few drops left. The last drops will disappear very quickly so be careful not to overheat the solution.
14. To get correct results in qualitative analysis, good organizational skills and techniques are essential to preventing cross contamination. Be sure to clean out and rinse glassware and to wipe stirring rods off between solutions. **Cross contamination** is one of the most common causes for false observations leading to incorrect conclusions.

## *How to Proceed with the Analysis*

### *Scenario*

A large industrial company is strongly suspected in the contamination of the local water supply with toxic heavy metals. The cause for the concern is a large holding ponds on its property. The usual monitoring system is in repair and the board of directors will pay you handsomely if you can identify the metals in their holding ponds. This could potentially save them from millions of dollars in legal fees. The criteria are that you must complete your analysis of known samples provided by the company's quality control team. This will provide the board the assurance they are seeking that you are indeed the right person for the task. Only then will the sample obtained from the holding pond be released for analysis.

The Qualitative Analysis you will be doing is that of Cation Analysis. You will work through a series of cation groups. The cations in each group are not related according to the periodic table but are related according to their similar analytical properties. You will separate the groups from each other according to the scheme given in the introduction. Once a group has been separated, work through the instructions to identify the individual cation(s). In many cases separations alone can be the identifier, particularly if there are no other ions that can separate or precipitate out along with your selected ion. If you suspect a particular ion from the separation scheme, you *should* do the confirmatory test. The confirmatory test for the particular ion of interest should provide reassurance.

**Note:** If you do not get a positive result for a cation from your separation scheme, then you do not have that cation. **DO NOT** continue to test for anything that gives a negative result. Move on as you do not have that cation. Testing for negative results is a waste of time. You will **not** have every cation from every group.

***Be sure to keep good records of what you have done and what you have observed. It is a good idea to come well prepared so that you do not waste precious time reading and looking for things.***

## Qualitative Analysis of Metal Cations

Table 1 indicates those metals involved in the qualitative analysis scheme. They include the:

- main group metals (Na, K, Mg, Ca, Ba, Al)
- transition metals (Cr, Mn, Fe, C, Ni, Cu, Zn; Ag, Cd, Hg).
- post-transition metals (Sn, Pb, Sb, Bi).

Other metals that fall into these groups are generally omitted from a qualitative analysis scheme due to their toxicity, (As, Tl), expense (Au, Pt), or their rarity (Li, Rb, Sr, Ga, etc).

A qualitative scheme for the analysis of cations separates cations into five groups as given in table 1. The analytical groups differ from the groups of the periodic table in that each group includes ions with similar analytical properties. Differentiation of the different groups is based upon differential precipitation properties between groups and among members of a group. In determining whether a cation will form a precipitate with a particular reagent, one can look in the K<sub>sp</sub> table (solubility product). The smaller the solubility product or the K<sub>sp</sub>, the more insoluble the ion.

**Table 1**

**Cation Groups for Qualitative Analysis**

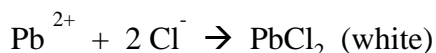
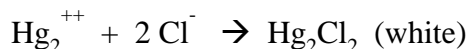
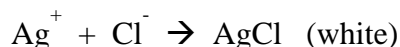
<i>Group</i>	<i>Cations</i>	<i>Precipitating Reagent/Conditions</i>
I	Ag <sup>+</sup> , Pb <sup>2+</sup> , Hg <sub>2</sub> <sup>2+</sup>	6M HCl
II	Cu <sup>2+</sup> , Bi <sup>3+</sup> , Hg <sup>2+</sup> , Cd <sup>2+</sup> , Sn <sup>2+</sup> , Sn <sup>4+</sup> , Sb <sup>3+</sup>	0.1M H <sub>2</sub> S, pH of 0.5
III	Al <sup>3+</sup> , Cr <sup>3+</sup> , Co <sup>2+</sup> , Fe <sup>2+</sup> , Mn <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup>	0.1M H <sub>2</sub> S, pH of 9
IV	Ba <sup>2+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup>	0.2M (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> , pH of 9.5
V	Na <sup>+</sup> , K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	No precipitates, separate tests for identification

In general, concentrations of reagents and pH are adjusted such that only one group is affected by the precipitating agent. Once a select group is precipitated out of solution, it is removed by first centrifuging the mixture to get all the precipitate out and then collecting the supernatant (potentially containing other groups) by a process called decanting. In a mixed solution, the supernatant can be further tested for other groups by selective precipitation and the remaining precipitate can be tested for Group members by further selective precipitation and confirmatory chemical tests.

## *Group I Cation Analysis*

Group I cations can be separated from the other groups since they form slightly soluble chlorides with the addition of hydrochloric acid. The other groups will remain in solution thus allowing the Group I chloride precipitates to be removed and further tested.

The precipitation reactions are:



### ***Procedure:***

**Note:** Because you will be collecting solutions and saving them in various tubes, you should not trust yourself to remember which is which. Be sure to **clearly label** your tubes. Do not discard any solutions or precipitates until you are sure you do not need them any longer.

1. Each person will receive approximately ~6 mL of unknown sample. **Record this unknown number - there is little your instructor can do for you if this number is lost.** The unknown sample will contain cations from all groups. To 3 mL of this sample (save the rest in case you have to repeat something) add 0.5 mL of 6M HCl. Stir well. The presence of a precipitate indicates the presence of one or more Group I cations. If no precipitate forms, there were no Group I cations present in the solution and you can proceed with testing for Group II cations. The 6M HCl is in excess and as a result the solution becomes slightly acidic. This prevents the precipitation of BiOCl if Bi<sup>3+</sup> from Group II is present in the unknown solution.
2. Centrifuge the solution in a balanced centrifuge and decant the supernatant into a separate tube. Test for completeness of precipitation by adding 1 drop of 6M HCl to the decanted supernatant. If precipitation is complete, store the liquid until testing for Group II can be performed. Label the tube i.e.: “further group testing”.
3. If precipitation is not complete, add a further 1 mL of 6M HCl and repeat the centrifugation process. Combine the precipitates and keep the supernatant for further Group II testing.

The precipitate containing one or more of the chlorides of Group I cations can now be analyzed.

4. To the precipitate, add approximately 5 mL of distilled water. Heat the contents in a boiling waterbath for 5 minutes **with stirring**. Centrifuge any remaining precipitate in a balanced centrifuge. Decant the supernatant to a different test tube leaving behind the

precipitate. Save the precipitate for further testing of  $\text{Ag}^+$  and  $\text{Hg}_2^{2+}$ . Lead(II),  $\text{Pb}^{2+}$ , is the only cation of Group I that is soluble in hot water. Therefore the supernatant must be tested for the presence of  $\text{Pb}^{2+}$ .

5. **Confirmation of the presence of lead (supernatant from step 4)**

If lead is present in your unknown, it will be in the supernatant. To the supernatant from step 4, add 2-3 drops of 6M acetic acid,  $\text{CH}_3\text{COOH}$  and 3-4 drops of 1M  $\text{K}_2\text{CrO}_4$ . The formation of the yellow precipitate of lead chromate,  $\text{PbCrO}_4$ , confirms the presence of lead. It may be necessary to centrifuge the solution in order to see the precipitate as it may be masked by the orange color of the  $\text{K}_2\text{CrO}_4$  reagent.

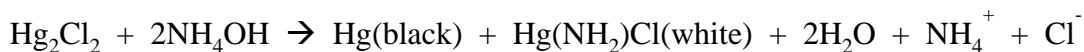
**Note:** If  $\text{Pb}^{2+}$  was present in your sample, then wash any remaining precipitate with ~2mL hot water again to remove all traces of  $\text{PbCl}_2$  as it may interfere with further tests.

6. **Confirmation of the presence of silver**

It is now necessary to consider the precipitate which may be comprised of  $\text{AgCl}$  or  $\text{Hg}_2\text{Cl}_2$  or a mixture of the two. By adding  $\text{NH}_4\text{OH}$  to the solution, the  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$  can be separated.

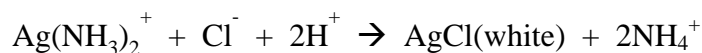


and



This type of reaction seen with  $\text{Hg}_2^{2+}$  is called a **disproportionation** reaction where the  $\text{Hg}_2\text{Cl}_2$  oxidizes and reduces itself to Hg (black) and  $\text{Hg}(\text{NH}_2)\text{Cl}$  (white). The mix of the two gives a grey precipitate that may be masked in the presence of white  $\text{AgCl}$  precipitate.

If the entire chloride precipitate dissolves, then only  $\text{AgCl}$  was in the precipitate as  $\text{Hg}_2\text{Cl}_2$  is not soluble in  $\text{NH}_4\text{OH}$ . If the white precipitate changes to black or grey, then  $\text{Hg}_2\text{Cl}_2$  was present but we do not yet know if there was any  $\text{AgCl}$ .  $\text{HNO}_3$  can be added to the supernatant once the precipitate and liquid have been separated. If  $\text{AgCl}$  is present, it will have dissolved and be in the liquid portion. Adding the nitric acid will cause the white  $\text{AgCl}$  to precipitate out according to the following reaction.



**Note:** If  $\text{Pb}^{2+}$  was present in your sample it may interfere with further tests.

Therefore to ensure the precipitate from step 4 is free of traces of  $\text{PbCl}_2$ , the remaining precipitate is washed with ~2mL hot water and isolated from the wash by filtration through Whatman paper. The wash is discarded. A clean testtube is positioned to collect the filtrate which may contain  $\text{Ag}(\text{NH}_3)_2^+$  when the precipitate is treated with 20 drops of **freshly prepared** 6M  $\text{NH}_4\text{OH}$ . If all the precipitate dissolves, then only  $\text{AgCl}$  was

present. If the precipitate becomes black or grey, due to the formation of Hg and  $\text{Hg}(\text{NH}_2)\text{Cl}$  then  $\text{Hg}_2^{2+}$  was present in the unknown.

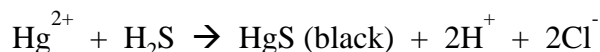
Regardless the filtrate collected is acidify to litmus with 6M  $\text{HNO}_3$  added dropwise until a white precipitate reappears, then  $\text{Ag}^+$  ion is confirmed present in the unknown.

7. Once you have decided which Group I cations your sample contains, then continue to test the solution saved in Step 2 for Group II cations. Submit your results for Group I on the report sheet provided.

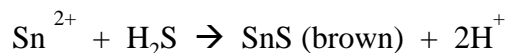
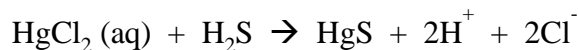
### *Group II Cation Analysis*

The Group II cations are chloride soluble ions and consequently they are readily separated from the slightly soluble Group I chloride insoluble cations. They can be further separated into groups through selective precipitation of a number of sulfides.  $\text{HgS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{SnS}$  and  $\text{SnS}_2$  precipitate from reaction with  $\text{H}_2\text{S}$  in 0.3M  $\text{H}^+$ . Because any of the Group I cations ( $\text{Ag}^+$  and  $\text{Hg}_2^{2+}$ ) have already been removed with the Group I precipitation, we do not have to worry about precipitation of  $\text{Ag}_2\text{S}$  or  $\text{Hg}_2\text{S}$ , even though they will react with  $\text{H}_2\text{S}$ . **Note:** Even though  $\text{Pb}^{2+}$  ions are precipitated and filtered off as  $\text{PbCl}_2$  in the Group 1 analysis, there may be enough residual  $\text{Pb}^{2+}$  in solution to precipitate as  $\text{PbS}$ . Consequently, many analytical schemes will place  $\text{Pb}^{2+}$  in both groups I and II.

None of the other sulfides of the other groups will precipitate out from  $\text{H}_2\text{S}$  at 0.3M  $\text{H}^+$  as they have high equilibrium constants. Consequently, by adding  $\text{H}_2\text{S}$  to the solution after the Group I cations have been removed and adjusting the pH to 0.3M  $\text{H}^+$ , we can remove  $\text{Hg}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  according to the following precipitation reactions:



**or**



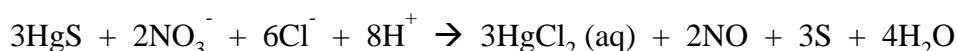
**and**



The precipitation procedure will result in a mixture of a number of sulfides. It is necessary to separate and identify the components of the sulfide mixture.

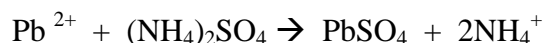
If Sn is present, or thought to be present, it is first necessary to treat the solution with a little  $\text{H}_2\text{O}_2$  in order to oxidize  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  before the Group II sulfides are precipitated by  $\text{H}_2\text{S}$ . Once the Group II cations are precipitated, SnS can be removed from the bulk by dissolving it in ammonium sulfide  $(\text{NH}_4)_2\text{S}$  as it is the only Group II sulfide that is soluble in ammonium sulfide. **Note: The company does not wish to test for tin.**

$\text{HgS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{PbS}$ ,  $\text{CdS}$  and  $\text{CuS}$  can be separated by differential solubility.  $\text{HgS}$  is insoluble in nitric acid while the rest of the group II cations are soluble. Therefore, when the sulfide precipitate is treated with  $\text{HNO}_3$ ,  $\text{HgS}$  and S should remain as a precipitate while the rest of the cations should remain in solution. Although  $\text{HgS}$  does not dissolve in  $\text{HNO}_3$ , it will dissolve in aqua regia ( $\text{HCl}$  and  $\text{HNO}_3$  mixed) and the resultant  $\text{HgCl}_2$  can be used to confirm its presence. The reaction equation is as follows:



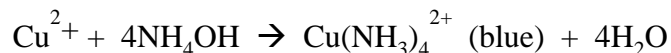
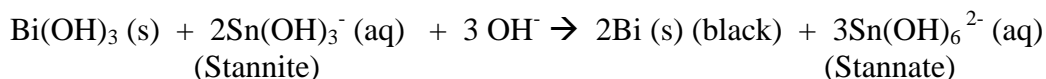
$\text{SnCl}_2$  (stannous chloride) is then added to the resultant  $\text{HgCl}_2$ .  $\text{Sn}^{2+}$  is oxidized to  $\text{Sn}^{4+}$  and **disproportionation** occurs when  $\text{HgCl}_2$  is reduced to  $\text{Hg}_2\text{Cl}_2(\text{s})$  (white) and  $\text{Hg}(\text{s})$  (black).

$\text{Pb}^{2+}$  can be removed from the cation mixture by precipitation with  $(\text{NH}_4)_2\text{SO}_4$  as  $\text{PbSO}_4$ . The  $\text{PbSO}_4$  can then be dissolved in ammonium acetate  $(\text{NH}_4\text{C}_2\text{H}_3\text{O}_2)$  and the lead precipitated out as yellow  $\text{PbCrO}_4$  upon reaction with  $\text{K}_2\text{CrO}_4$ .

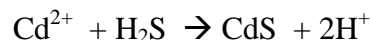
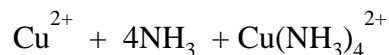


$\text{Bi}^{3+}$  can be removed from  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  by the addition of  $\text{NH}_4\text{OH}$  to the solution.  $\text{Bi}^{3+}$  forms a white precipitate ( $\text{Bi}(\text{OH})_3$ ) while  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  remain in solution. Reaction of  $\text{Bi}(\text{OH})_3$  with sodium stannite gives rise to black elemental bismuth. The  $\text{Cu}(\text{NH}_3)_4^{2+}$  formed, when copper is present, gives the solution a blue color.

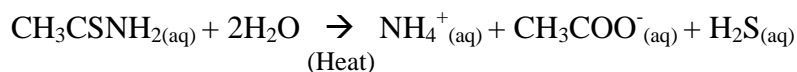
Separation of  $\text{Cu}^{2+}$  from  $\text{Cd}^{2+}$  is done by the reduction of  $\text{Cu}^{2+}$  to elemental copper using sodium dithionite as a reducing agent. Reaction of the isolated cadmium with thioacetamide gives rise to the yellow sulfide precipitate of  $\text{CdS}$ .



**or**

**Procedure:**

**Note:** H<sub>2</sub>S gas is an **extremely** poisonous gas. Rather than exposing students to this toxic gas, H<sub>2</sub>S will be generated from thioacetamide in solution.



It is **VERY IMPORTANT** that any steps using thioacetamide be contained in the hood. If you are transporting a test tube that has just been reacted with thioacetamide to another hood, be sure that you stopper the tube before taking it out of the hood. **DO NOT** breathe the gas as it is a very harmful irritant to the lungs. Pour any solutions containing H<sub>2</sub>S down the drains in the hood followed by lots of running water.

1. The supernatant from step 1 in Group I analysis should contain any of the Group II cations if they are present. Use approximately 3-4 mL of the supernatant solution for testing.
2. To precipitate the HgS, CuS, CdS, Bi<sub>2</sub>S<sub>2</sub> and PbS, it is necessary to make the solution 0.3M with respect to H<sup>+</sup>. The Group III cations (Ni<sup>2+</sup>, Zn<sup>2+</sup>, etc.) will remain in solution.

Add 15 drops of concentrated NH<sub>4</sub>OH. Test the pH with red litmus paper to determine if it is alkaline.

**Note:** Red litmus paper turns blue in a basic solution.

If the solution is not alkaline, add 6M NH<sub>4</sub>OH dropwise until it is alkaline to red litmus paper. Do not be concerned if a precipitate forms as the solution changes pH. When checking the litmus paper, look at the outer edge of the drop where the liquid wicks away from the solid to determine if the litmus paper has changed otherwise the color may be masked by the presence of the precipitate.

3. Now add 6M HCl dropwise until the solution is barely acidic to blue litmus paper. This should require no more than 1-3 drops of acid. Now add 1 drop of 6M HCl for every mL of solution. Since one drop of 6M HCl is approximately 0.05 mL, this should make the solution 0.3 M with respect to H<sup>+</sup>.
4. Go to the hood containing the thioacetamide and add 1 mL. Heat the solution for five minutes (uncorked) in a boiling water bath in the fumehood. **DO NOT** heat with the cork

in as the cork and contents of the tube will blow out of the tube when the pressure builds up inside.

5. Lightly cork and centrifuge the solution in a balanced centrifuge for approximately 1 minute to remove the Group II cations as sulfide precipitates. **If your solution is a mixture, then save the supernatant for further analysis of groups 3, 4, and 5.**
6. The precipitate from step 5 should contain the Group II sulfide precipitates, HgS (black), Bi<sub>2</sub>S<sub>3</sub> (brownish-black), CuS (black), PbS (black) and CdS (yellow).

**Note:** Sulfide precipitates are not that stable so you should plan your work so that you are able to stop when everything is in solution. It is best not to save sulfide precipitates, but if you must, be sure to cover them with a layer of distilled water.

It is necessary to wash the sulfide precipitate from Step 5 free of Cl<sup>-</sup> because although HgS is insoluble in HNO<sub>3</sub>, it is soluble in aqua regia (HCl + HNO<sub>3</sub>). If Cl<sup>-</sup> is present, then when HNO<sub>3</sub> is added aqua regia will be formed and Hg will be missed as it becomes solubilized. To do this, add approximately 3 mL distilled H<sub>2</sub>O. Stopper the tube and shake vigorously to dislodge the precipitate. Centrifuge and discard the supernatant. Repeat the wash procedure twice more.

7. HgS can be separated from the other group II sulfide precipitates by dissolution in HNO<sub>3</sub>. Suspend the precipitates in the 1 mL of H<sub>2</sub>O by vigorous shaking. Add 1 mL of 6M HNO<sub>3</sub> to the suspended sulfides. Heat the mixture gently to almost boiling for approximately 5 minutes to ensure the Group II sulfides, except HgS, have been dissolved by the HNO<sub>3</sub>. If HgS is present, a precipitate should remain. If all the precipitate dissolves, then there was no HgS present. Cool the solution in cold tap water and centrifuge for 1 minute. Decant the supernatant liquid to a new test tube and stopper. Save for isolating other group II cations. Test the precipitate for mercury.

If a dark colored precipitate remains, it is indicative of HgS. It is possible to miss HgS though, if it is obscured by nearly white free sulfur or if HgS has been converted into a light colored double salt Hg(NO<sub>3</sub>)<sub>2</sub>·2HgS by the HNO<sub>3</sub>. Therefore, if a precipitate remains after dissolution by HNO<sub>3</sub> in step 6, the confirmatory test for Hg should be carried out on the precipitate.

**Confirmatory Test for Mercury**

8. To the precipitate remaining in step 7, add 6 drops of concentrated 6M HNO<sub>3</sub> and 6 drops of 6M HCl. This makes aqua regia or “royal water”. Heat in a boiling water bath until the reaction is complete (the precipitate dissolves and the bubbling stops leaving a clear or milky solution). A small ball of free sulfur may remain and this needs to be removed using a glass stirring rod. Centrifuge and discard any precipitate that may remain.
9. To the aqua regia solution above, add 1 mL of distilled water and transfer all the solution to an evaporating dish. **In the hood**, very carefully heat the solution on a hotplate and evaporate it to the size of a quarter. It is important not to evaporate the solution to dryness as the Hg<sub>2</sub>Cl<sub>2</sub> is volatile and maybe lost.

**Note:** Mercuric chloride vapors are poisonous and therefore be careful not to breathe in any of the vapors.

10. Cool the solution in the evaporating dish and divide it in two. To half the solution, add 0.5 mL of 0.1M SnCl<sub>2</sub> dropwise. If Hg<sup>2+</sup> is present, a white precipitate of Hg<sub>2</sub>Cl<sub>2</sub> will form. This somewhat glossy precipitate will turn dark or grey with time as the Hg<sup>2+</sup> is reduced to free Hg by excess Sn<sup>2+</sup>

To the other half of the solution, immerse a piece of heavy copper wire in the liquid for a couple of minutes. If mercury is present, it will be deposited as shiny liquid mercury on the copper wire as Hg<sub>2</sub>Cl<sub>2</sub> is reduced to free Hg.

11. The supernatant saved in step 7 contains the other Group II cations. To this solution add 3 drops of concentrated NH<sub>4</sub>OH and 10 drops of saturated ammonium sulfate solution. The presence of a precipitate is indicative of the presence of lead.
12. Centrifuge the solution and separate the precipitate from the supernatant. The precipitate should be tested for the presence of lead and the supernatant saved for further Group II cation separatory tests. Lead is the only Group II cation that will form insoluble sulfate precipitates.

**Optional: Test to ensure what is isolated is of Lead**

13. Dissolve the precipitate in approximately 0.5 mL ammonium acetate solution (NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>). To the resultant solution, add 2 drops 1M K<sub>2</sub>CrO<sub>4</sub>. A yellow precipitate of PbCrO<sub>4</sub> is indicative of the presence of lead. Maybe omitted if confirmed in Group I.
14. To the supernatant from step 12 add concentrated ammonium hydroxide dropwise until it is alkaline to red litmus paper. Once it is alkaline, add 3-5 drops excess concentrated NH<sub>4</sub>OH. The appearance of a deep blue color in the solution is indicative of the presence of the copper amine complex, Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>. If a white precipitate appears, it is most likely Bi(OH)<sub>3</sub>. Because a small amount of precipitate may be masked by a large amount of Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> the solution should be gently warmed in a water bath and then centrifuged to

check for the presence of precipitate. The presence of a white precipitate is indicative of  $\text{Bi}(\text{OH})_3$  and the confirmatory test for bismuth should then be done. Keep the supernatant for further Group II testing.

15. ***Confirmatory test for the presence of Bismuth***

If a white precipitate occurs in step 14, then  $\text{Bi}^{3+}$  is likely present. First wash the precipitate twice with 1 mL distilled water each time. Centrifuge and discard the washes.

16. Prepare a **fresh solution** of sodium stannite by adding 6M NaOH dropwise to 2 mL of 0.1M  $\text{SnCl}_2$ . A thick white precipitate of  $\text{Sn}(\text{OH})_2$  will form and persist. Add 6M NaOH dropwise to dissolve the precipitate and give a strongly basic solution. At the point where the precipitate **just** dissolves, then the sodium stannite is done. Add all the freshly prepared sodium stannite to the white precipitate from step 14. Sodium stannite acts as a reducing agent and will reduce  $\text{Bi}^{3+}$  to metallic Bi causing the precipitate to turn black.

17. The supernatant in step 14 contains the remaining Group II ( $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ) cations. If the supernatant is blue, this is indicative of the presence of  $\text{Cu}^{2+}$ .

The presence of  $\text{Cd}^{2+}$  however, cannot be ruled out, as its clear color will be masked by the presence of  $\text{Cu}^{2+}$ . The absence of a blue color indicates the absence of  $\text{Cu}^{2+}$  but does not confirm the presence of  $\text{Cd}^{2+}$ . If the solution is clear, proceed with the confirmatory test for  $\text{Cd}^{2+}$  (step 20). If the solution is blue, then test for both the copper and cadmium (steps 18 & 20 respectively).

18. Remove a few drops from the solution in step 17 to another test tube and save it for the second confirmation test for copper. To the remaining solution, add a pinch of  $\text{Na}_2\text{S}_2\text{O}_4$  (sodium dithionite\*) and heat gently for five minutes in a boiling waterbath. Observe the color of the precipitate that may form. If no precipitate forms or if the solution remains faintly blue, add a little more sodium dithionite and reheat. Be careful not to add an excess of the sodium dithionite or overheat as the cadmium may be lost to other side reactions. The presence of a dark precipitate indicates the reduction of  $\text{Cu}^{2+}$  to metallic copper.

\* $\text{Na}_2\text{S}_2\text{O}_4$  - sodium dithionite solid may cause fire if wetted please use a dry scoopula.

19. If the solution in step 17 was blue but no precipitate was obtained in step 18, then using the saved solution (beginning of step 18), proceed to the second confirmatory test for copper in step 21.

**Confirmatory of Cadmium**

20. Decant the supernatant into another test tube and test for the presence of cadmium. To this solution, add 5 drops of thioacetamide and heat for five minutes in a boiling waterbath. The presence of a yellow precipitate is CdS. If a dark precipitate occurs and copper was found previously, this is residual copper forming the CuS precipitate. If this occurs, dissolve the precipitate in HNO<sub>3</sub> (as previously), neutralize it and then make it basic (as above) and then repeat the dithionite treatment again to test for cadmium.

**Confirmatory Test for Copper**

21. To the “saved” blue solution in step 18, add 6M acetic acid dropwise until the solution becomes acidic to blue litmus paper. Once it is acidic, add a few drops of 0.1M potassium ferrocyanide (K<sub>4</sub>Fe(CN)<sub>6</sub>). If copper is present, a maroon precipitate of Cu<sub>2</sub>Fe(CN)<sub>6</sub> will appear.

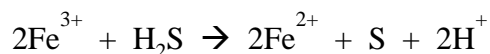
**Results:**

Prepare in a flow diagram summarizing your results for the separation and identification of Group I and II cations. Be sure to include your unknown number and the positive cations present in your unknown. Use correct formulas for reagents and products in all parts of the flow diagram. Be sure to include observations (i.e. precipitate, colour, etc.)

Submit your results for Group II on the report sheet provided.

**Group III Cation Analysis**

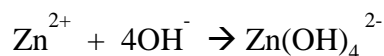
The cations of Group III do not form slightly soluble chlorides and do not form sulfides through precipitation by H<sub>2</sub>S in 0.3M H<sup>+</sup>. Some sulfides however, that are not precipitated by H<sub>2</sub>S in 0.3M H<sup>+</sup>, will be precipitated by H<sub>2</sub>S when the H<sup>+</sup> concentration is lowered or base is added before treatment. Zn<sup>2+</sup>, Fe<sup>2+</sup>/Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup> and Al<sup>3+</sup> fall into this category. If such a treatment is done to a solution containing these Group III cations, the following precipitates may be observed: ZnS (white), NiS (black), FeS (black), Fe(OH)<sub>3</sub> (reddish-brown), Cr(OH)<sub>3</sub> (blue-green) and Al(OH)<sub>3</sub> (white). If the cation analysis of the unknown has been carried on from Group II analysis, most of the Fe<sup>3+</sup> and Cr<sup>6+</sup> will have been lost in the treatment of the unknown solution by acidic H<sub>2</sub>S according to the following reaction.



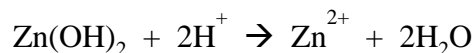
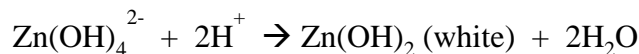
Consequently it is unlikely the precipitates of these oxidation states will be present.

Once the sulfides and hydroxides have been precipitated, they can be separated from the solution through centrifugation. The precipitate is then treated with a  $\text{SO}_4^{2-}/\text{HSO}_4^-$  buffer solution with an  $\text{H}^+$  concentration in the order of  $10^{-2}$  M. This mildly acidic solution will dissolve  $\text{FeS}$ ,  $\text{Cr}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  but not  $\text{NiS}$  and  $\text{ZnS}$ . When the solution is centrifuged, the precipitate should contain any  $\text{NiS}$  and  $\text{ZnS}$  present, while the supernatant should contain the dissolved  $\text{Fe}^{2+}/^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$ .

The precipitate containing  $\text{NiS}$  and  $\text{ZnS}$ , can be dissolved in aqua regia. Excess  $\text{NaOH}$  is then added to the dissolved  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  resulting in the precipitation of pale green  $\text{Ni}(\text{OH})_2$  leaving the zinc in solution as  $\text{Zn}(\text{OH})_4^{2-}$  ( $\text{Zn}(\text{OH})_2$  is amphoteric). The equations for the reactions are:

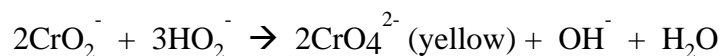
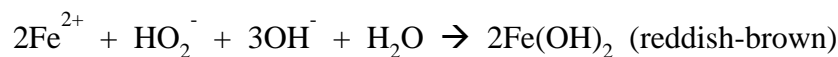


Centrifugation will separate the solution and precipitate. The solution is kept for testing for  $\text{Zn}$  and the precipitate tested for  $\text{Ni}$ .  $\text{H}_2\text{S}$  treatment of the supernatant will precipitate white  $\text{ZnS}$  or alternatively treatment with  $\text{HCl}$  will precipitate white  $\text{Zn}(\text{OH})_2$  which will then dissolve in excess  $\text{HCl}$ .



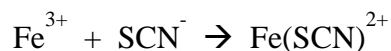
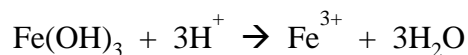
Treatment of the blue-green precipitate by dimethylglyoxime should precipitate red nickel(II) dimethylglyoxime.

The supernatant saved earlier should contain any  $\text{Fe}^{2+/3+}$ ,  $\text{Cr}^{3+}$  or  $\text{Al}^{3+}$  present. Treatment of this solution with excess  $\text{NaOH}$  and  $\text{H}_2\text{O}_2$  will result in the oxidation of  $\text{Fe}^{2+}$  and  $\text{Cr}^{3+}$  to reddish-brown  $\text{Fe}(\text{OH})_3$  and  $\text{CrO}_4^{2-}$  according to the following reactions:



$\text{Al}^{3+}$  that may be present, will end up in solution as  $\text{Al}(\text{OH})_4^-$  (aluminate ions). White  $\text{Al}(\text{OH})_3$  is not precipitated due to its amphotericity. Blue-green  $\text{Cr}(\text{OH})_3$  is also amphoteric and dissolves in excess  $\text{OH}^-$  forming chromite ions ( $\text{CrO}_2^-$  and  $\text{Cr}(\text{OH})_4^-$ ) which are then oxidized by the peroxide to chromate ions ( $\text{Cr}^{6+}$ ).

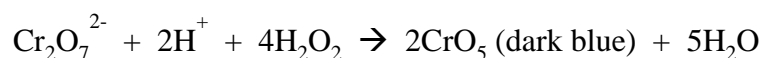
Reaction of the reddish-brown precipitate with potassium thiocyanate,  $\text{KSCN}$ , should yield a dark red solution of  $\text{Fe}(\text{SCN})^{2+}$  according to the following reaction:



The solution containing the aluminate ions,  $\text{Al}(\text{OH})_4^-$ , is adjusted to the proper  $\text{H}^+$  concentration thus resulting in the precipitation of  $\text{Al}(\text{OH})_3$ .



If a yellow-orange solution occurs at this point, it is indicative of the presence of Cr in the +6 oxidation state.  $\text{Cr}^{6+}$  reacts in an acidic environment in the presence of peroxide to form the highly blue-colored peroxy complex  $\text{CrO}_5$ . This complex will further decompose in  $\text{H}_2\text{O}$  to  $\text{Cr}^{3+}$  and  $\text{O}_2$ . An overall simplified reaction is given below.



### ***Procedure:***

1. To 3mL of the unknown, either one containing only Group III cations or the supernatant left over from separating Group I and II cations from a mixture, add 15 drops of 5M  $\text{NH}_4\text{Cl}$ . Make the solution alkaline by adding 15 drops of concentrated  $\text{NH}_4\text{OH}$ . Check with red litmus to ensure it is alkaline and then add an excess of 10 drops concentrated  $\text{NH}_4\text{OH}$ . The absence of a precipitate indicates there is no  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$  present. Check carefully though, because white finely divided  $\text{Al}(\text{OH})_3$  may be very difficult to see.
2. In the fumehood, add 1 mL of thioacetamide and heat in a hot water bath for 5 minutes. Check for precipitation. When precipitation appears to be completed, centrifuge to separate the two phases. Pour the supernatant into a fresh test tube and test for completeness of precipitation by adding 2 drops of concentrated  $\text{NH}_4\text{OH}$  and 0.5 mL thioacetamide. If no more precipitate appears save and label the supernatant liquid for Group IV. Combine any precipitates.
3. Wash the precipitate with 3 mL of distilled water by adding the  $\text{H}_2\text{O}$ , mixing well to suspend and then centrifuging to remove the  $\text{H}_2\text{O}$ . Discard the wash water.
4. Add 3 mL of the  $\text{SO}_4^{2-}/\text{HSO}_4^-$  buffer prepared fresh by mixing equal volumes of saturated  $\text{Na}_2\text{SO}_4$  and 2M  $\text{NaHSO}_4$  to the washed precipitate. The remaining precipitate will contain any  $\text{NiS}$  and  $\text{ZnS}$  while the supernatant will contain dissolved  $\text{FeS}$ ,  $\text{Cr}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$ . Stir the buffer and precipitate for several minutes to ensure complete dissolution of the above precipitates.

5. Centrifuge and decant the supernatant into a clean test tube and ensure complete dissolution of the precipitate by adding another mL of the buffer to any remaining precipitate. Centrifuge and combine the supernatants. Keep the precipitate for testing of Ni and Zn. Stopper the supernatant and save for testing of  $\text{Fe}^{2+/3+}$ ,  $\text{Cr}^{3+}$  &  $\text{Al}^{3+}$  in step 10.
6. Wash the precipitate that remains from step 5 by adding 3 mL of distilled  $\text{H}_2\text{O}$  to the precipitate and suspending. Centrifuge and discard the wash. Add 2 mL of aqua regia prepared by adding 1 mL 6M HCl and 1 mL 6M  $\text{HNO}_3$  to the washed precipitate. Suspend the precipitate by mixing and boil the solution in a hot water bath for a few minutes. A lump of free sulfur may form and this should be broken up so that it does not coat any of the precipitate and protect it from the aqua regia. This treatment should dissolve any NiS or ZnS present, so once the solution is cooled and centrifuged, any remaining precipitate can be discarded as it should be just free sulfur. Transfer the supernatant containing the Ni and/or Zn to a clean test tube.
7. To the supernatant from step 6, add 6M NaOH dropwise until the solution is alkaline to red litmus paper. Add 1 mL of excess NaOH. Because of its amphoteric nature, if  $\text{Zn}^{2+}$  is present, it may first precipitate as white  $\text{Zn}(\text{OH})_2$  and then redissolve as  $\text{Zn}(\text{OH})_4^{2-}$ . If nickel is present a pale green precipitate of  $\text{Ni}(\text{OH})_2$  will appear. If there is no precipitate, then Ni is not present. If all the precipitate doesn't dissolve, warm gently and cool to ensure all the Zn is in solution. Centrifuge the solution and separate any precipitate from the supernatant. Test the precipitate for Ni and the supernatant for Zn.

### ***Confirmatory test for nickel***

8. If there is a pale green precipitate, confirmation of  $\text{Ni}(\text{OH})_2$  presence can be done by dissolving the precipitate in a minimum amount of 6M HCl (this means adding 6M HCl dropwise until the precipitate just dissolves). Once dissolved, make the solution slightly alkaline to red litmus paper with 6M  $\text{NH}_4\text{OH}$ . Add a few drops of alcoholic dimethylglyoxime,  $\text{C}_4\text{H}_8\text{O}_2\text{N}_2$ . If nickel is present, a red solution of nickel(II) dimethylglyoxime,  $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$  should appear. If it doesn't appear initially, acidify the solution with  $\text{CH}_3\text{COOH}$  and then add  $\text{NH}_4\text{OH}$  drop by drop. Once an optimum  $\text{H}^+$  concentration is reached, red  $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$  will appear if nickel is present. If this doesn't happen, there is no nickel in the solution.

### ***Confirmatory test for zinc***

9. The supernatant from step 7 should be tested for the presence of Zn. Divide this solution into two parts. In the fumehood, to one part add 15 drops of thioacetamide and heat in a hot water bath for 5 minutes. If Zn is present, a white precipitate of ZnS will appear. If a very dark precipitate appears, dissolve it in 1 mL of cold 1M HCl. If any precipitate remains, centrifuge and discard. Adjust the solution to an alkaline pH using 3M  $\text{NH}_4\text{OH}$  and repeat the thioacetamide step above. Any Zn present will appear as a white or greyish precipitate. If no precipitate occurs, then you can proceed to the second confirmatory step just to insure the Zn hasn't been missed.

Acidify the other portion of the supernatant from step 7 using 3M HCl. Do this slowly dropwise and observe carefully after each addition until the solution is just acidic to blue litmus paper. Any  $\text{Zn(OH)}_4^{2-}$  will precipitate out as white  $\text{Zn(OH)}_2$  initially and then redissolve when excess acid is added. If 6M NaOH is carefully added in a dropwise manner, white  $\text{Zn(OH)}_2$  will reprecipitate and then dissolve in excess NaOH.

10. Transfer the solution from step 5, potentially containing  $\text{Fe}^{2+/3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$  to an evaporating dish. Concentrate the volume to approximately 1 mL by gently boiling. Cool the solution and neutralize with 6M NaOH. **Note:** A neutral solution will result in red litmus paper being red and blue litmus paper remaining blue when tested.

When the solution is neutralized, add 1 mL excess 6M NaOH. If the solution turns green, it may be indicative of the presence of chromite ions.

11. To the cooled solution, add 1 mL of 3%  $\text{H}_2\text{O}_2$  and heat to boiling for 2 minutes and then keep the solution hot for approximately 5 minutes to ensure the  $\text{H}_2\text{O}_2$  is completely decomposed. A red precipitate is indicative of  $\text{Fe(OH)}_3$ . Cool the solution and centrifuge to separate any precipitate. Pour the supernatant through filter paper set in a small buret funnel and collect it in a clean test tube and leaving the precipitate in the test tube. The red precipitate should be tested for  $\text{Fe(OH)}_3$  and the collected filtrate tested for  $\text{CrO}_4^{2-}$  and  $\text{Al(OH)}_4^-$ . If there is no precipitate, then Fe is absent from the unknown. However any precipitate obtained here should be tested for Fe.

### ***Confirmatory Test for the Presence of Iron***

12. Add 1 mL of 6M HCl, 2 mL of  $\text{H}_2\text{O}$  and a few drops of 1M KSCN to a test tube. Add this solution to the remaining precipitate from step 11 to this solution. The appearance of a dark red color due to the production of  $\text{Fe(SCN)}^{2+}$  complex ion confirms the presence of iron.

### ***Confirmatory Test for the Presence of Aluminum***

13. To the filtrate collected in step 11, potentially containing  $\text{CrO}_4^{2-}$  and  $\text{Al(OH)}_4^-$ , add 6M HCl until the solution is just acidic to blue litmus paper. Add 3M  $\text{NH}_4\text{OH}$  until the solution is just basic to red litmus paper. Be sure to monitor these steps carefully in order to get the pH into the right range. Warm the solution in a hot water bath for a few minutes and centrifuge to collect any precipitate. Any  $\text{Al(OH)}_4^-$  originally present should be converted to white  $\text{Al(OH)}_3$ . If no precipitate occurs, double check by adding 5 drops of 6M  $\text{NH}_4\text{OH}$ , warm again in a hot water bath and the centrifuge to collect the precipitate. If there is no white precipitate at this point then there was no  $\text{Al(OH)}_4^-$  in the filtrate. Do not discard any supernatant as you will be discarding  $\text{CrO}_4^{2-}$  that potentially may be present.

**Confirmatory Test for the Presence of Chromium**

14. If  $\text{CrO}_4^{2-}$  is present, the solution from step 13 should be yellow or orange in color. Acidify the supernatant solution from step 13 with 6M HCl. This will convert any  $\text{CrO}_4^{2-}$  to  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{HCrO}_4^-$ . Add a few drops of 3%  $\text{H}_2\text{O}_2$  to the acidified solution. The appearance of a dark blue peroxy complex,  $\text{CrO}_5$ , is indicative of the presence of Cr.

**Results:**

In a flow diagram prepare a summary of your results for the separation and identification of Group III cations. Be sure to include your unknown number and the positive cations present in your unknown. Use correct formulas for reagents and products in all parts of the flow diagram. Be sure to include observations (i.e. precipitate, colour, etc.)

Submit the report sheet for Group III Analysis

**Groups IV Cation Analysis**

In a mixture of group cations, Groups IV and V will remain in solution after Groups I, II and III have been removed because their chlorides, sulfides and hydroxides are still soluble enough after the other group precipitation conditions. Group IV cations form insoluble carbonates and this principle is used to separate them from Group V cations. Group V cations form soluble carbonates.

It turns out that the elements of Group IV also happen to belong to the same periodic table group. As a result they have very similar physical properties making them more difficult to distinguish from each other than the ions in the other groups.

**Procedure:**

Your unknown sample will contain Group IV elements.

**Group IV Cations**

1. To 3 mL of your unknown add 50 mg  $\text{NH}_4\text{Cl}$ . Stir the solution to dissolve the ammonium chloride
2. If the solution is acidic, carefully neutralize it with 15 M  $\text{NH}_4\text{OH}$  to litmus. Add one extra drop of ammonium hydroxide to make the solution slightly basic.
3. Add 20 drops of 3M  $(\text{NH}_4)_2\text{CO}_3$  and warm the solution in a hot water bath ( $\sim 60^\circ\text{C}$ ) for five minutes to complete the precipitation. Do not use a boiling water bath as this will drive off the ammonia. A precipitate should occur. If it doesn't then add a few more drops of the  $(\text{NH}_4)_2\text{CO}_3$ .

4. Centrifuge the solution to separate supernatant which may contain  $\text{Mg}^{2+}$  from the other 2 Group IV precipitates. Save the supernatant for testing.
5. To the remaining precipitate in step 4, add 5 drops of 6M acetic acid to dissolve the precipitate. Stir and place in a warm water bath until the  $\text{CO}_2$  ceases to evolve. This will dissolve the calcium and barium carbonates. If the precipitate does not dissolve, then add 6M acetic acid dropwise and repeat the procedure until it does.

### ***Confirmatory Test for Barium***

6. To the dissolved carbonates, add 10 drops of 1.5M  $\text{K}_2\text{CrO}_4$ . Observe what happens.
7. Centrifuge the solution and decant the supernatant to a new test tube. Save the precipitate for further testing. This separates the barium from the calcium.
8. To further confirm the presence of barium, convert the barium chromate to barium sulfate. Wash the precipitate with 1 mL of distilled water and then dissolve it in a few drops of 3M HCl. Add 10 drops of water and remove a few drops of the solution to a small test tube for the flame test below. To the remaining solution add 4 drops of 3M  $\text{H}_2\text{SO}_4$ . The formation of a white precipitate is indicative of the presence of barium sulfate.

### ***Confirmatory Test for Calcium***

9. Neutralize the supernatant solution saved in step 7 with concentrated ammonia. To the neutral solution, add several drops of 0.25 M ammonium oxalate. A white precipitate of calcium oxalate should form if calcium is present. If no precipitate forms, check the pH of the solution. Oxalates are acid soluble, so if the pH isn't correct, they will not precipitate out of solution.

### ***Confirmatory Test for Magnesium***

10. To the supernatant saved in step 4, add about 50 mg of  $\text{Na}_2\text{HPO}_4$ . If a precipitate does not form immediately, scratch the side of the test tube with a stirring rod and let the mixture stand in warm water for a few minutes.
11. A white, crystalline precipitate of  $\text{MgNH}_4\text{PO}_4$  should form to confirm the presence of Magnesium.

### ***Group V Cations (the soluble group V cations will not be)***

12. The supernatant from step 10 should contain the remaining Group V cations, mainly the sodium and potassium ions. The ammonium ion will be dealt with on its own.

**Note:** The ammonium ion is a formal member of the Group V ions, but is introduced as a contaminant in the separation of the other ions. Consequently a positive result on separated solutions will often be obtained. Ammonium ion is therefore tested using the original unknown sample to which no ammonia or ammonium salts have been added as reagents. We will not test for the ammonium ion in this lab.

13. Sodium and potassium form very few precipitates as almost all sodium and potassium compounds are water soluble. As a result, their presence is generally detected by a flame test. Follow the procedure for flame tests below on the supernatant solution from step 12.
14. To determine if a solution contains one of the other ions or a mixture of the two, the flame tests need to be performed with and without cobalt glasses. Compare your flame results to single ion standard solutions and to a standard mixed sodium and potassium solution.

The sodium flame colour predominates over other flames and consequently the flame should be observed first without cobalt glasses and then with cobalt glasses to remove the predominant sodium flame colour.

### ***Flame Tests***

Flame tests are not routinely used on Group IV cations but they are interesting to see. Test the calcium-containing supernatant in step 8 and the dissolved barium in step 9. Compare your results to flame tests of prepared standard single ion solutions.

1. Clean the end of a nichrome wire (attached to a glass rod) by dipping it into concentrated HCl and heating it to a red glow in the hottest part of a flame (tip of the inner blue cone). Repeat the HCl treatment until the wire imparts no colour when burned in the flame.
2. Dip the end of the loop into one of the solutions and then hold in at the end of the flame (not in the hottest part of the flame). Note the colour of the flame. Repeat the procedure looking through cobalt glass and note whether there is a colour change.

***Test all solutions in this manner.***

### ***Results***

Submit the report sheets for Group IV.

Lastly a final report is required and should include a comprehensive flow chart for the complete separation and identification of the Groups I to IV metal contents found in the holding pond. Include pertinent balanced confirmation reactions, significant observations, in some cases relevant flame test results should be included. Your instructor will provide you with more information in class regarding the final report.

<b><u>Group I cation(s):</u></b>	
Name: _____	Date: _____
Section: _____	
Sample (Unknown) Number: _____	
Result: _____	

**/ 5**

<b><u>Group III cation(s):</u></b>	
Name: _____	Date: _____
Section: _____	
Sample (Unknown) Number: _____	
Result: _____	

**/ 15**

**Group II cation(s):**

Name: \_\_\_\_\_ Date: \_\_\_\_\_

Section: \_\_\_\_\_

Sample (Unknown) Number: \_\_\_\_\_

Result: \_\_\_\_\_

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**Group IV cation(s):**

Name: \_\_\_\_\_ Date: \_\_\_\_\_

Section: \_\_\_\_\_

Sample (Unknown) Number: \_\_\_\_\_

Result: \_\_\_\_\_

**/ 10**

**Holding pond sample (18/12/2007):**

**Sample Number:** \_\_\_\_\_.

**Group I:** \_\_\_\_\_.

**Group II:** \_\_\_\_\_.

**Group III:** \_\_\_\_\_.

**Group IV:** \_\_\_\_\_.

Name: \_\_\_\_\_ Date: \_\_\_\_\_

Section: \_\_\_\_\_

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