Chapter 14 – The Analysis of A Solution for Ag (I), Pb (II) and Hg (I) Ions

NAME:

Lab Section:

Date:

Sign-Off:

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Introduction

As this is an introduction into the marvelous realm of cation analysis in "Qualitative Analysis", it seems reasonable to begin with what metals and their ions we're going to be examining. The table, below, summarizes the ions in their ANALYTICAL groups -- NOT groups from the periodic table:

ANALYTICAL Groups				
Group 1	Group 2	Group 3	Group 4	Group 5
Metals: Ag, Pb, Hg	Metals: Bi, Cu, Pb, Hg	Metals: Ni, Co, Fe, Al, Zn	Metals: Ca, Sr, Ba	Metals: Mg
Ionic forms: Ag+, Pb^{2+}, Hg_2^{2+}	Ionic forms: Bi^{3+}, Cu^{2+}, Pb^{2+}, Hg^{2+}	Ionic forms: Ni^{2+}, Co^{2+}, Fe^{2+}, Al^{3+}, Zn^{2+}	Ionic forms: Ca^{2+}, Sr^{2+}, Ba^{2+}	Ionic forms: Mg^{2+}

This grouping is not inclusive and is intended to serve only as an introduction.

These groups were organized after observing that these ions were separable in specific groups by specific reagents (chemicals in solution). How best to approach this? Well, keep in mind that you can't just go out and buy a bottle of a cation or an anion. You have to buy a SALT -- remember those things? When you put a salt in water, it dissociates into a cation and an anion. In this case, we're interested in the cations. If all of these cations were in solution, could we separate them into the groups, above? The answer is YES. Here's how it works: A mixture of the ions is treated with HCl. When this happens, a precipitate is formed. When analyzed, the precipitate is a mixture of AgCl, Hg_2Cl_2 and $PbCl_2$ -- all chloride salts of these ions. These ions are the first separated out as insoluble precipitates (remember the solubility rules?) and are in Group 1. The supernatant (the liquid left behind after centrifugation) contains the remaining ions.

To that supernatant, acid and some form of hydrogen sulfide is added. Generally, a hydrogen sulfide "generator" such as thioacetamide is used. The mixture is boiled and another precipitate is formed. In this instance the precipitate consists of Bi_2S_3, CuS, As_2S_3, Sb_2S_3, SnS, HgS. These ions (called the acid-sulfides) are the second separated out as insoluble precipitates (remember the solubility rules?) and are in Group 2. The supernatant (the liquid left behind after centrifugation) contains the remaining ions.

To THAT supernatant, ammonia and hydrogen sulfide is added and heated. The precipitate contains a mixture of NiS, CoS, MnS, FeS, Al_2S_3, Cr_2S_3 and ZnS -- the ammoniacal sulfides. These ions are the third separated out as insoluble precipitates (remember the solubility rules?) and are in Group 3. The supernatant (the liquid left behind after centrifugation) contains the remaining ions.

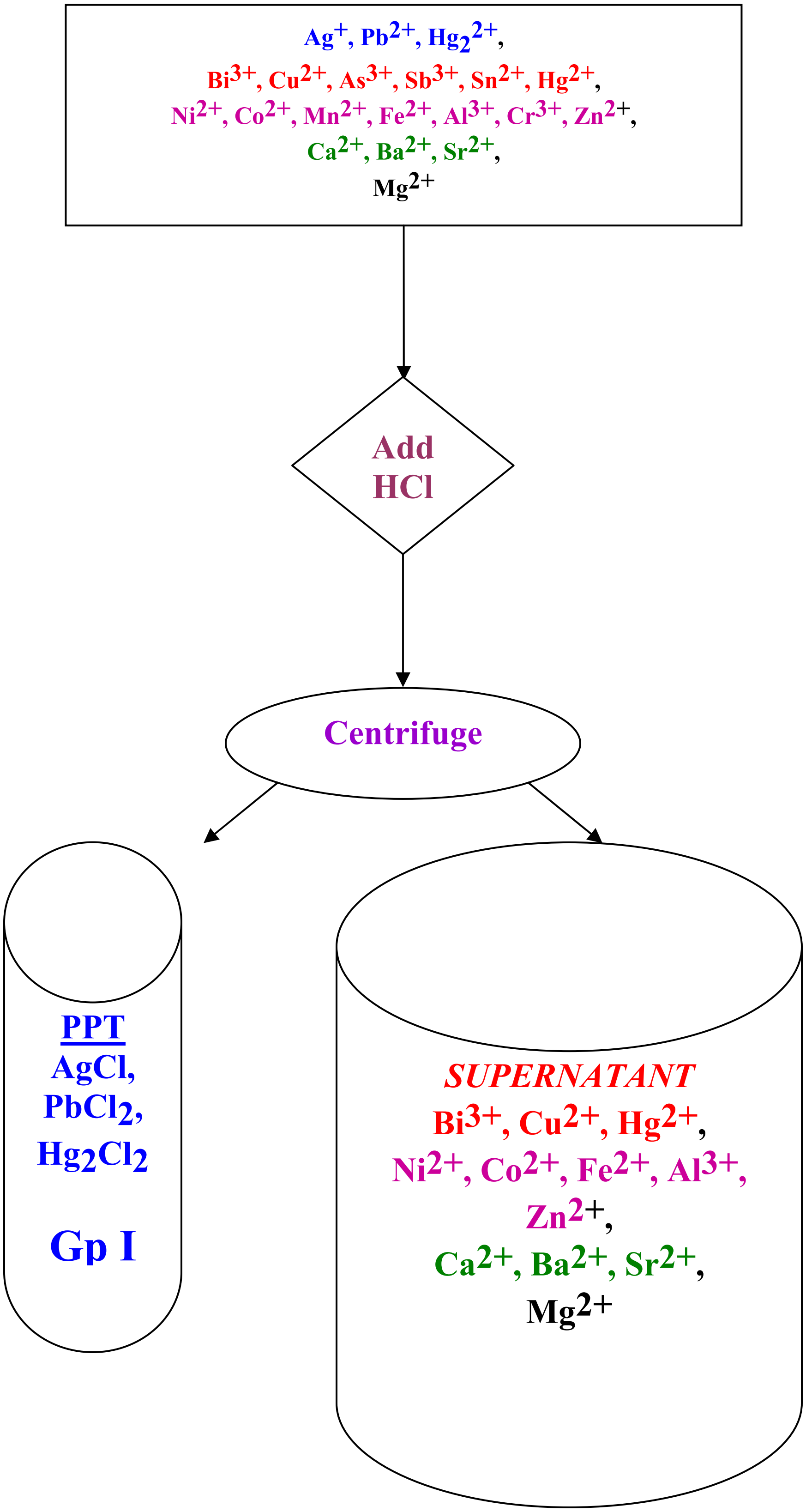
To that supernatant, ammonia and carbonate are added. The precipitate contains a mixture of $SrCO_3$, $BaCO_3$ and $CaCO_3$ -- the carbonates. These ions are the fourth separated out as insoluble precipitates (remember the solubility rules?) and are in Group 4. The supernatant (the liquid left behind after centrifugation) contains the remaining ion.

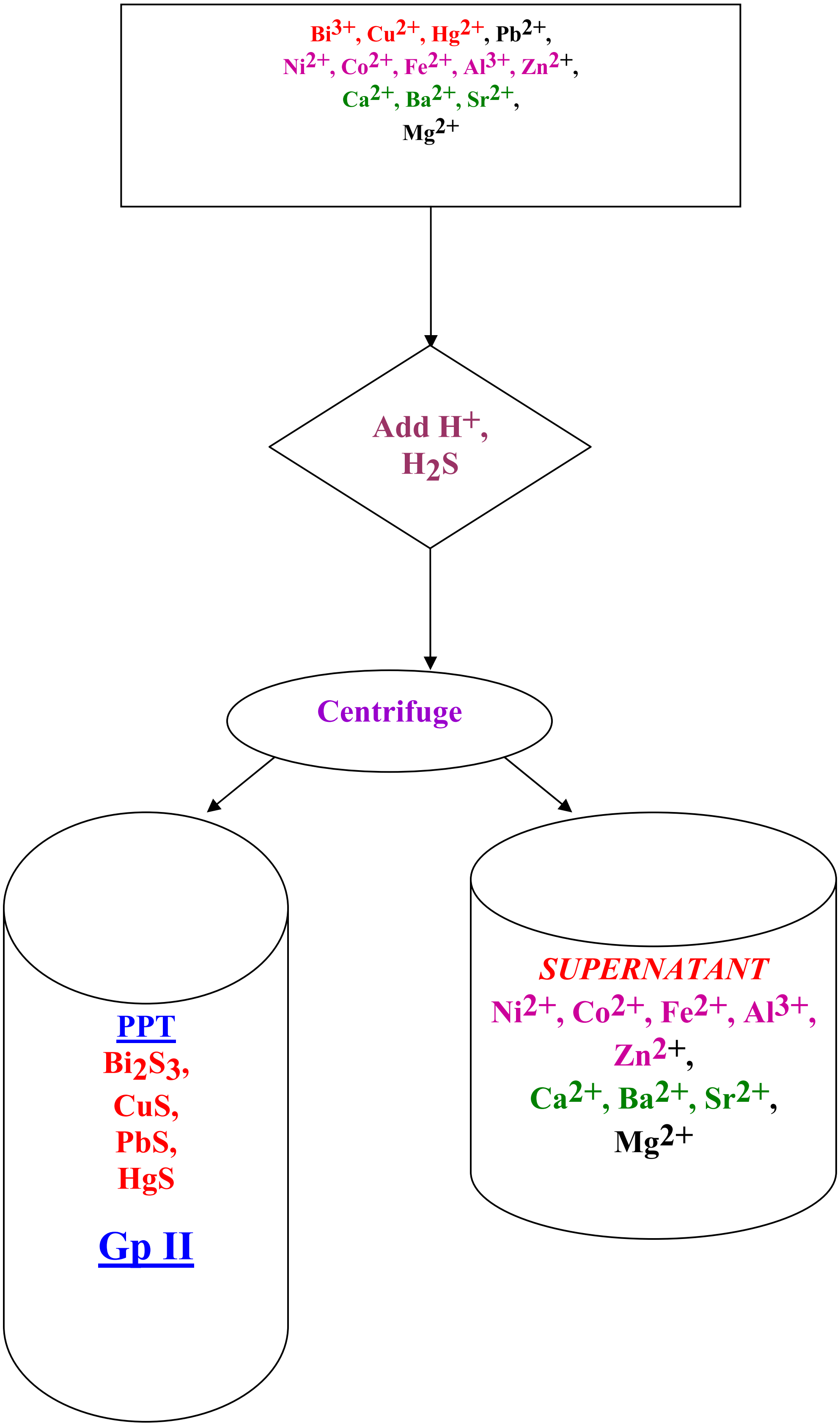
Since there is only one ion (in our example), we need not precipitate it as all five groups are now separated. This last group is called the soluble group. This is what you will be introducing yourselves to in lab this.

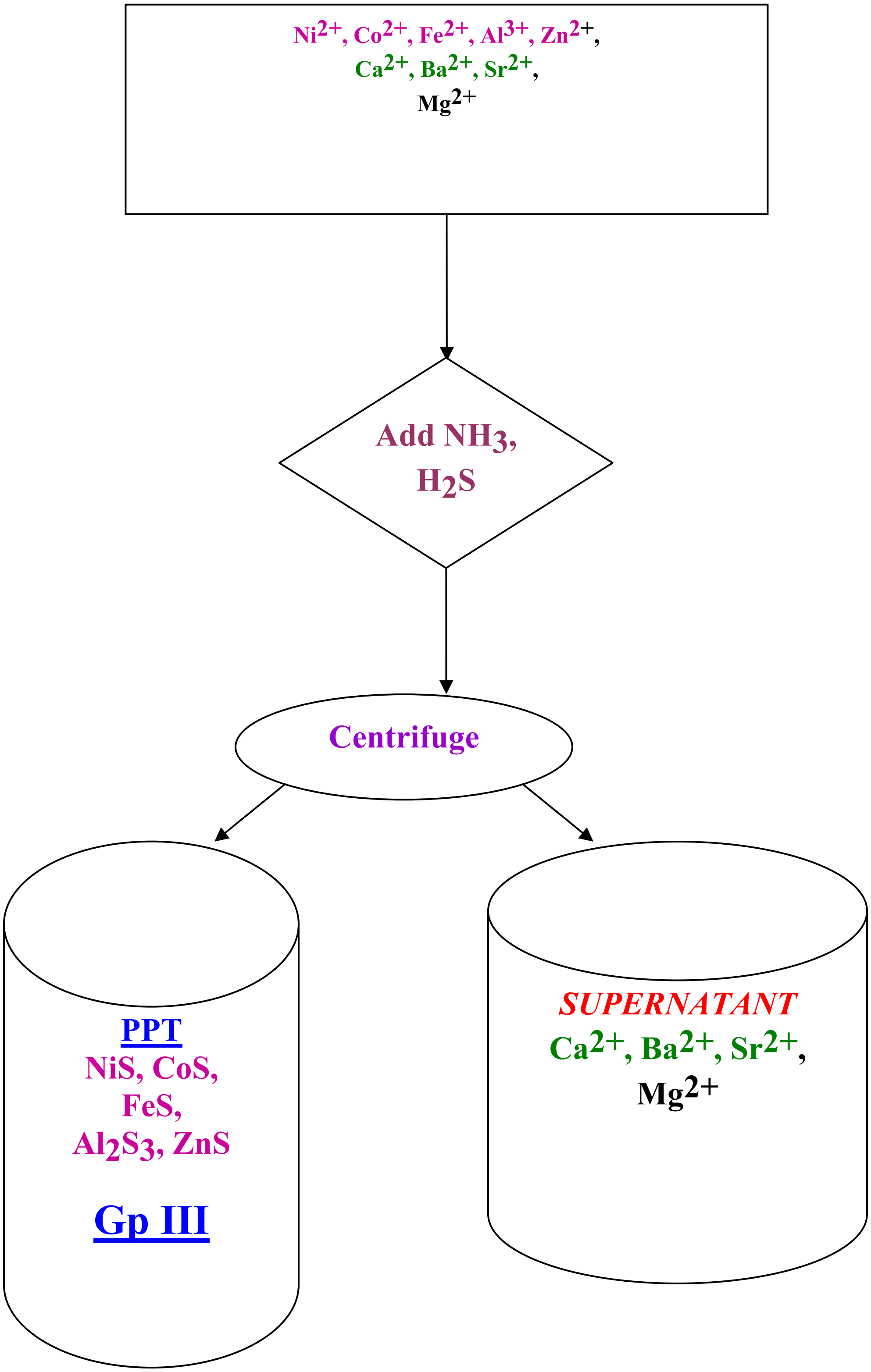
The following 4 pages illustrate a very simplified set of flow charts (after King and Noyes*) showing the separation of 5 groups of cations based on their chemical reactive properties (per above) – your outlines will have more detail and will focus on the separation of each ion from its analytical group.

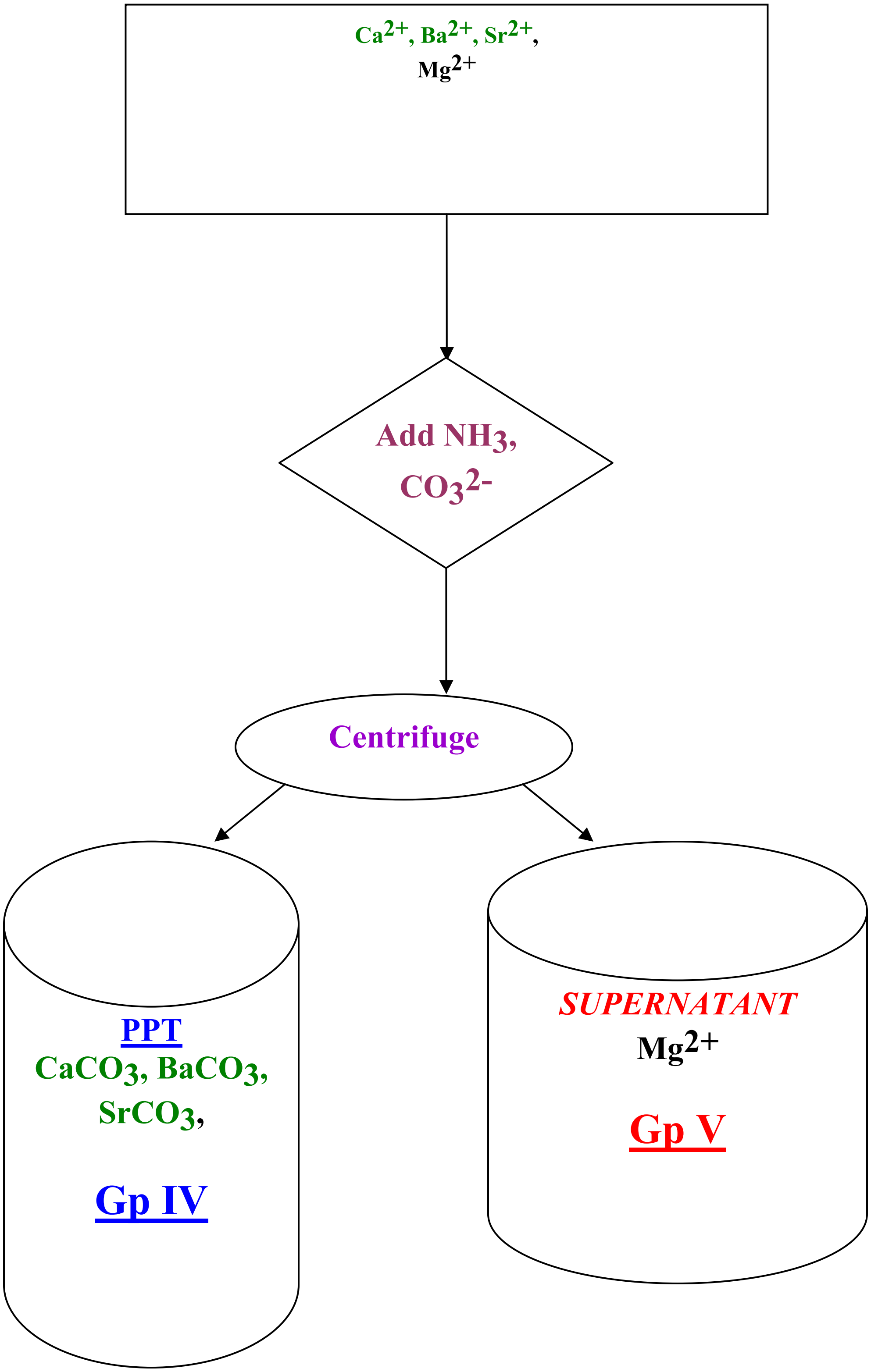
*King, E.J.: **Qualitative Analysis and Electrolytic Solutions**. (Harcourt, Brace and World: New York) © 1959.

*Noyes, A.A.: **Qualitativ Chemical Analysis.** (The Macmillan Company: New York) © 1915.


Ag^{+}, Pb^{2+}, Hg_2^{2+},
Bi^{3+}, Cu^{2+}, As^{3+}, Sb^{3+}, Sn^{2+}, Hg^{2+},
Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}, Al^{3+}, Cr^{3+}, Zn^{2+},
Ca^{2+}, Ba^{2+}, Sr^{2+},
Mg^{2+}
Add HCl
Centrifuge
PPT
$AgCl$,
$PbCl_2$,
Hg_2Cl_2
Gp I
SUPERNATANT
Bi^{3+}, Cu^{2+}, Hg^{2+},
Ni^{2+}, Co^{2+}, Fe^{2+}, Al^{3+},
Zn^{2+},
Ca^{2+}, Ba^{2+}, Sr^{2+},
Mg^{2+}


Bi^{3+}, Cu^{2+}, Hg^{2+}, Pb^{2+},
Ni^{2+}, Co^{2+}, Fe^{2+}, Al^{3+}, Zn^{2+},
Ca^{2+}, Ba^{2+}, Sr^{2+},
Mg^{2+}
Add H^{+},
H_2S
Centrifuge
PPT
Bi_2S_3,
CuS,
PbS,
HgS
Gp II
SUPERNATANT
Ni^{2+}, Co^{2+}, Fe^{2+}, Al^{3+},
Zn^{2+},
Ca^{2+}, Ba^{2+}, Sr^{2+},
Mg^{2+}


Ni^{2+}, Co^{2+}, Fe^{2+}, Al^{3+}, Zn^{2+},
Ca^{2+}, Ba^{2+}, Sr^{2+},
Mg^{2+}
Add NH_3, H_2S
Centrifuge
PPT
NiS, CoS, FeS, Al_2S_3, ZnS
Gp III
SUPERNATANT
Ca^{2+}, Ba^{2+}, Sr^{2+},
Mg^{2+}


Ca^{2+}, Ba^{2+}, Sr^{2+},
Mg^{2+}
Add NH_3,
CO_3^{2-}
Centrifuge
PPT
$CaCO_3$, $BaCO_3$,
$SrCO_3$,
Gp IV
SUPERNATANT
Mg^{2+}
Gp V

The Metals: Ag, Pb, Hg

Ag -- Silver

Horn silver is silver chloride. Tarnished silver is silver sulfide (Ag_2S). Typically, silver is obtained as a by-product of other metals. It is a white lustrous metal. Its polished surface reflects light. It is the best conductor of heat and electricity other than gold. It's not used as such as it's too expensive for that. It is malleable (can be pounded out into a flat sheet) and ductile (can be drawn into a wire). It is used for coins, silverware and ornaments. Sterling silver is about 7.5% Cu. Jewelry silver is 20% copper. It has been used in dentistry in amalgam filling; it is used in photography and mirrors. It is also used to stop bleeding after calves are polled and has been used in solution to scarify tissue in the nasal cavity for those susceptible to epistaxis.

Pb -- Lead

Lead pipes lead to Rome's downfall -- pun intended. Galena is fool's silver and is lead sulfide. It is the heaviest of the metals except for mercury and gold. Tetraethyl lead [$Pb(C_2H_5)_4$] is a catalytic converter poison and was used in leaded gasoline to prevent knocking. Pb is used in car batteries. Lead is used in stained glass windows. It is no longer used in pigments for paints, nor is it used in solders, much. Silver has replaced it in many solders.

Hg -- Mercury

Both 1^+ and 2^+ forms are considered, here. Aristotle called this liquid silver or quicksilver. It's used to extract gold due to the high solubility of gold in mercury. It's a silvery white metal and is the only metal in the liquid state at room temperature. It has enjoyed wide-spread use in thermometers. That is changing as we learn more and more how dangerous even a little mercury can be. It is not used as much in dentistry to make amalgam fillings (Note: whenever you read "amalgam", think mercury). It is used in mercury vapor lamps and fluorescent lamps. Hg_2Cl_2 is calomel -- used in calamine lotion. $HgCl_2$ is corrosive sublimate and is very toxic. Mercury salts have been used as antiseptics -- not so much any more. Mercury is a cumulative poison. A fatal dose is 0.2-0.4 g (200-400 mg). The treatment, at least initially, is to give egg whites and milk (both contain proteins with LOTS of SH groups that LOVE Hg and remove it from binding with proteins in the GI tract).

Experimental

This specific experiment sets the stage for the next four (4) experiments. While you will be running known samples of each of the known groups individually, i.e., when you do Group I, you'll have only Group I cations in your known sample, *ad nauseum*, you'll also be running an unknown sample that has cations from ALL five analytical groups side-by-side with the known. It is of paramount importance that you label carefully, keep copious notes and follow experimental details carefully. Every effort has been made to streamline these experiments in the interest of time, clarity and brevity. Remember, too, to set out your separation outline for Group I cations so you can move right along, efficiently and effectively.

The Separation of the Ions of Analytical Group I

Obtain a sample of Group I known cations and an unknown sample. Make certain each tube is labeled appropriately so you can keep track of the experiments you perform on each sample – be sure to run them side-by-side – this is so you can observe what the positive results look like and can compare them to your unknown sample. A flow chart to clarify the text follows this page.

To both samples, add 6M HCl a drop at a time with mixing. Permit the precipitate (ppt) to settle between drops, as you want to obtain the total precipitate without re-solubilizing the chlorides in the presence of excess HCl.

Once you have obtained all the ppt, place each tube in the centrifuge (across from each other) and spin the tube for about a minute. Pour the supernatant (super) from the unknown sample ONLY off into another tube and label it "❷S2". You need not save the super from the known solution, i.e., discard it in the inorganic chemical waste container provided in the lab.

To the two tubes that contain ppt, add about 5 drops (gtts) of hot distilled water and heat in a boiling water bath for a couple of minutes. Immediately centrifuge the hot samples and pour off the super as quickly and carefully as possible into new tubes labeled "Pb super".

Combine the two Pb super tubes, add 1 gtt HOAc and 4 gtts potassium chromate. A bright yellow ppt is positive for lead(II).

To the 2 original tubes containing ppt, add 3-5 gtts of concentrated ammonia with mixing. Centrifuge and separate the super from the ppt. A black or dark grey ppt is positive for mercury(I). Make the super acidic to litmus paper with 6M nitric acid. A white ppt is positive for silver(I).

Dispose of all of your waste as directed by your professor. Store your "❷S2" tubes sealed in Parafilm in the test tube rack provided in lab. Clean up your lab bench and glassware before you leave the lab. Remember to complete the problems immediately following prior to next week's lab.

⓿I Obtain a sample of Group I known cations and an unknown sample. Make certain each tube is labeled appropriately so you can keep track of the experiments you perform on each sample – be sure to run them side-by-side – this is so you can observe what the positive results look like and can compare them to your unknown sample.

↓

❶T To both samples, add 6M HCl a drop at a time with mixing. Permit the precipitate (ppt) to settle between drops, as you want to obtain the total precipitate without re-solubilizing the chlorides in the presence of excess HCl. Once you have obtained all the ppt, place each tube in the centrifuge (across from each other) and spin the tube for about a minute.

↙ ↘

❷P To the two tubes that contain ppt, add about 5 drops (gtts) of hot distilled water and heat in a boiling water bath for a couple of minutes. Immediately centrifuge the hot samples and pour off the super as quickly and carefully as possible into new tubes labeled "❸S".

❷S Pour the supernatant (super) from the unknown sample ONLY off into another tube, seal with Parafilm and label it "❷S 2". Store in the test tube rack provided in lab. (Discard the super from the known solution in the inorganic chemical waste container provided in the lab.)

↙ ↘

❸P To the 2 original tubes (❷P) containing only ppt, now, add 3-5 gtts of concentrated ammonia with mixing. Centrifuge and separate the super (❹S) from the ppt. **<u>A black or dark grey ppt is positive for mercury(I).</u>**

❸S Combine the two "❸S" tubes, add 1 gtt HOAc and 4 gtts potassium chromate. **<u>A bright yellow ppt is positive for lead(II).</u>**

↓

❹S Make the super acidic to litmus paper with 6M nitric acid. **A white ppt is positive for silver(I).**

Problem Set – Cations: Ag (I), Pb (II) and Hg (I)

1. Draw a one page flow diagram showing how you separated these cations and your results.

2. Use the periodic table that you utilized for the anions and color the cations from this group in a single color (different from that used for the anions).

3. Give the electronic configuration of Ag°, Hg°, Pb°; Ag^+, Hg^{2+}, Pb^{2+}.

4. What is it about these cations that renders them similar enough to be in this group?

5. If the dissociation of calomel is as follows:

$$Hg_2Cl_2 \Leftrightarrow Hg_2^{2+} + 2Cl^-$$

determine the solubility of the calomel under the following conditions: 0.25 M HCl.

6. Given the following reaction:

$$BaF_2 + CrO_4^{2-} = BaCrO_4 + 2F^-$$

(K_{sp} BaF_2 = 1 x 10^{-6}; K_{sp} $BaCrO_4$ = 1.2 x 10^{-10}). Calculate the equilibrium constant from the K_{sp}'s. Will any BaF_2 form if $BaCrO_4$(s) is shaken with a solution that is 0.0005M in CrO_4^{2-} and 0.001M in F^-?

References/Sources/Bibliography

King, E.J.: **Qualitative Analysis and Electrolytic Solutions**. (Harcourt, Brace and World: New York) © 1959.

Noyes, A.A.: **Qualitativ Chemical Analysis.** (The Macmillan Company: New York) © 1915.

Slowinski, E.J. and Masterton, W.L.: **Qualitative Analysis and the Properties of Ions in Aqueous Solution.** (W.B. Saunders Company: Philadelphia) © 1971.