Chapter 17 – The Analysis of A Solution for Ca (II), Sr (II) and Ba (II) Ions

NAME:

Lab Section:

Date:

Sign-Off:

Chapter 17 – The Analysis of A Solution for Ca (II), Sr (II) and Ba (II) Ions

Introduction

All members of this group are silvery-white, crystalline metals that are malleable and ductile.

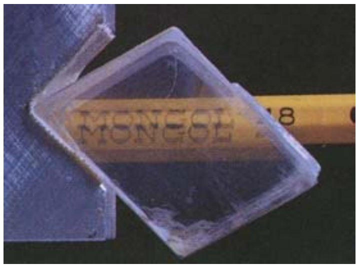
Ca – Calcium

Calcium is used in dehydrating agents; alloyed with Si; used in bearings and in storage battery grids. Is harder than Pb and has a dark red flame.

Compounds of significance include CaO (unslaked lime or quicklime), $Ca(OH)_2$ (slaked lime; hydrated quicklime), saturated $Ca(OH)_2$ (limewater) and a suspension of $Ca(OH)_2$ (milk of lime).

In caves, calcium reacts with bicarbonate to form calcium carbonate and water and CO_2. Stalactites hang from the ceiling and stalagmites grow up from the floors in limestone caves.

Calcite ($CaCO_3$) precipitates at temperatures less than 30°C. It has the property of birefringence (double refraction): when a beam of light enters calcite, it is split into two beams and two images are observed:



The reaction of 3-4 parts sand with 1 part calcium hydroxide, 1 part water and CO_2 from the air produces $CaCO_3$ and water. This reaction is the reaction that occurs between mortar (between bricks) and CO_2 that is in the air. It takes hundreds of years to form (think about the castles of Germany that are 400-600 years old and still standing), making mortar very time efficient.

Sr – Strontium

Sr salts are used in fireworks and flares to produce bright carmine colors. ^{90}Sr was a fallout product of atomic bombs of the type used in WW II. Sr is in Group II on the

Period Table -- same as Ca – and caused a lot of osteogenic sarcoma. Is about as hard as Pb and has a carmine flame.

Ba – Barium

Barium used to be used in vacuum tubes -- if you're old enough to remember them. It is also used in spark plugs. Is softer than Pb and has a yellow/green flame. $BaSO_4$ is used in studies of the GI tract (upper GI, lower GI [Ba enema], Ba swallow, small bowel series). Although $BaSO_4$ is extremely poisonous it is so insoluble that it is of a non-poisonous nature for medical use.

Experimental

As in previous experiments, obtain a sample of the known cations and the sample of super from the previous experiment for the unknown sample. Run both side-by-side. A flow chart follows the discussion, again.

To the known and unknown samples, add concentrated ammonia until the solution is alkaline to litmus – go slowly and carefully, i.e., a drop-at-a-time. Once the solution is appropriately alkalinized, add 1 mL of 3M ammonium carbonate with stirring/mixing/vortexing. Following the mixing, add enough ethanol (reagent alcohol) or methanol to double the volume in the test tube – if there is not enough room in the tube, split the contents between 2 tubes. Set the tube[s] in an ice bath and stir for 10 minutes. Centrifuge the mixture.

Set the super aside. Treat the ppt with 0.5 mL 3M ammonium carbonate and centrifuge. Add the super from this step to the first super, label (❷S5), seal and store until Group V is studied.

Treat the just obtained ppt with a minimum of 6M acetic acid in a hot water bath – heat for 3-5 minutes to accelerate the dissolution of the ppt. Once the ppt has dissolved, add about 1 mL 3M ammonium acetate with stirring. Add a drop at a time 0.5M potassium chromate until precipitation is complete. Centrifuge, setting the super aside for the moment. A yellow ppt is positive for Ba(II).

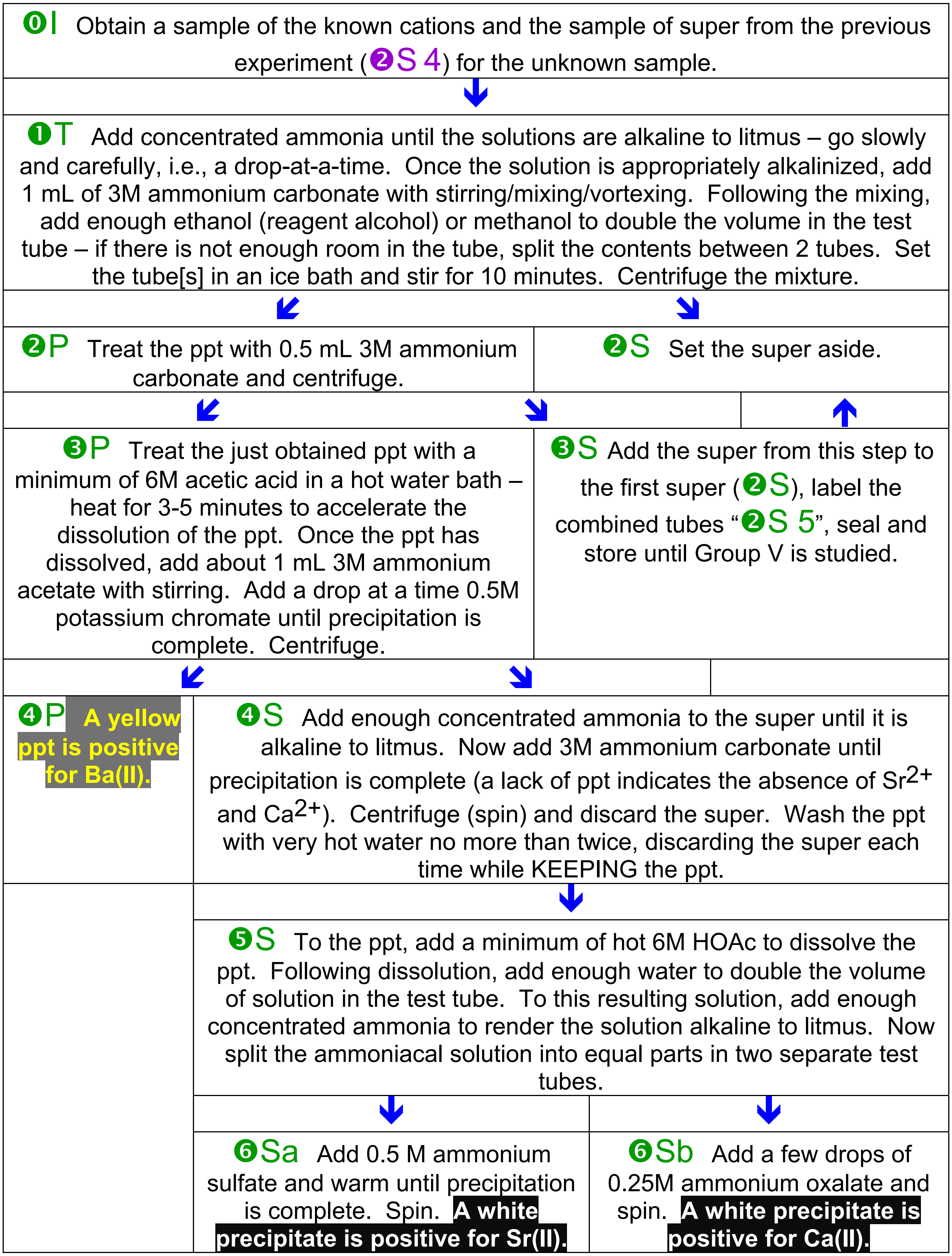
Go back to the super you set aside momentarily. Add enough concentrated ammonia to the super until it is alkaline to litmus. Now add 3M ammonium carbonate until precipitation is complete (a lack of ppt indicates the absence of Sr^{2+} and Ca^{2+}). Centrifuge (spin) and discard the super. Wash the ppt with very hot water no more than twice, discarding the super each time while KEEPING the ppt.

To the ppt, add a minimum of hot 6M HOAc to dissolve the ppt. Following dissolution, add enough water to double the volume of solution in the test tube. To this resulting solution, add enough concentrated ammonia to render the solution alkaline to litmus. Now split the ammoniacal solution into equal parts in two separate test tubes.

To the first tube, add 0.5 M ammonium sulfate and warm until precipitation is complete. Spin. A white precipitate is positive for Sr(II).

To the second tube, add a few drops of 0.25M ammonium oxalate and spin. A white precipitate is positive for Ca(II).

The flow chart and problem set follow.



⓿I Obtain a sample of the known cations and the sample of super from the previous experiment (❷S 4) for the unknown sample.

❶T Add concentrated ammonia until the solutions are alkaline to litmus – go slowly and carefully, i.e., a drop-at-a-time. Once the solution is appropriately alkalinized, add 1 mL of 3M ammonium carbonate with stirring/mixing/vortexing. Following the mixing, add enough ethanol (reagent alcohol) or methanol to double the volume in the test tube – if there is not enough room in the tube, split the contents between 2 tubes. Set the tube[s] in an ice bath and stir for 10 minutes. Centrifuge the mixture.

❷P Treat the ppt with 0.5 mL 3M ammonium carbonate and centrifuge.

❷S Set the super aside.

❸P Treat the just obtained ppt with a minimum of 6M acetic acid in a hot water bath – heat for 3-5 minutes to accelerate the dissolution of the ppt. Once the ppt has dissolved, add about 1 mL 3M ammonium acetate with stirring. Add a drop at a time 0.5M potassium chromate until precipitation is complete. Centrifuge.

❸S Add the super from this step to the first super (❷S), label the combined tubes "❷S 5", seal and store until Group V is studied.

❹P **A yellow ppt is positive for Ba(II).**

❹S Add enough concentrated ammonia to the super until it is alkaline to litmus. Now add 3M ammonium carbonate until precipitation is complete (a lack of ppt indicates the absence of Sr^{2+} and Ca^{2+}). Centrifuge (spin) and discard the super. Wash the ppt with very hot water no more than twice, discarding the super each time while KEEPING the ppt.

❺S To the ppt, add a minimum of hot 6M HOAc to dissolve the ppt. Following dissolution, add enough water to double the volume of solution in the test tube. To this resulting solution, add enough concentrated ammonia to render the solution alkaline to litmus. Now split the ammoniacal solution into equal parts in two separate test tubes.

❻Sa Add 0.5 M ammonium sulfate and warm until precipitation is complete. Spin. **A white precipitate is positive for Sr(II).**

❻Sb Add a few drops of 0.25M ammonium oxalate and spin. **A white precipitate is positive for Ca(II).**

Problem Set – Cations: Ca (II), Sr (II) and Ba (II)

1. Draw a one page flow diagram of what you did with Group IV cations and your results.

2. Do the periodic table thing in your anion problem set for these cations.

3. If the silver ion had not been removed from the solution with HCl in Group I precipitation, would the silver ion have precipitated as silver sulfide?

4. If the equilibrium constant for:

$$PbS + 2HOAc \rightarrow Pb(OAc)_2 + H_2S$$

is 1 X 10^{-30}, and if R = 0.001987 Kcal/mol·K at 25°C, calculate the Gibbs free energy for this reaction. Will the reaction proceed as written? Why or why not?

5. If a solution is 0.01M in Sr^{2+} and Ba^{2+} ions, what per cent of Ba^{2+} remains unprecipitated before $SrSO_4$ precipitates following the addition of sodium sulfate to the solution? K_{sp} for barium sulfate = $1.08X10^{-10}$; K_{sp} for strontium sulfate = $2.8X10^{-7}$.

6. If a solution is 0.05M in Ag^+ and Hg_2^{2+} ions, what percent of Hg_2^{2+} remains unprecipitated before AgCl precipitates following the addition of HCl to the solution? K_{sp} for silver chloride = $1.8X10^{-10}$; K_{sp} for mercurous chloride = $1.3X10^{-18}$.

7. If a solution is 0.025M in Al^{3+} and Co^{2+} ions, what per cent of Al^{3+} remains unprecipitated before $Co(OH)_2$ precipitates following addition of NaOH to the solution? K_{sp} for aluminum hydroxide = $1.4X10^{-34}$; K_{sp} for cobalt hydroxide = $2X10^{-16}$.

8. How many *drops* (remember 1 mL = 20 drops; ∴ 1 gtt = 0.05 mL) of 1M HOAc are required to dissolve 5 mg $SrCO_3$?

9. How many drops of 3M HNO_3 are required to dissolve 12 mg $CaCO_3$?

10. How many drops of 6M H_2SO_4 are required to dissolve 35 mg Na_2CO_3?

11. If ammonia combines with water as shown below and the K_i (ionization constant) = $1.8X10^{-5}$,

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

calculate the $[OH^-]$ if the solution in which you are working is 0.4M in NH_3 and 0.3M in NH_4^+.

12. Is this enough OH^- (in the previous question) to precipitate Mg^{2+} as $Mg(OH)_2$ if the $[Mg^{2+}]$ is 0.01M?

13. Is there enough OH^- (in the previous question) to precipitate Cd^{2+} as $Cd(OH)_2$ if the $[Cd^{2+}]$ is 0.0025M?

14. Is there enough OH^- (in the previous question) to precipitate Fe^{3+} as $Fe(OH)_3$ if the $[Fe^{3+}]$ is 0.0005M?

15. Design a quick and simple method to determine if the blue/green solution is $Cu(NH_3)_4^{2+}$ or $Ni(NH_3)_6^{2+}$.

References/Sources/Bibliography

Baskerville, C. and Curtman, L.J.: **A Course in Qualitative Chemical Analysis**. (The Macmillan Company: New York) © 1915.

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

Lagowski, J.J. and Sorum, C.H.: **Introduction to Semimicro Qualitative Analysis, Seventh Edition.** (Prentice Hall: Englewood Cliffs) © 1991.

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.

Wismer, R.K.: **Qualitative Analysis with Ionic Equilibrium**. (Macmillan Publishing Company: New York) © 1991.