Identification of an Unknown Metal Sulfate Hydrate by Determination of the Percent Water and Percent Sulfate

INTRODUCTION

In this experiment, you will be given an unknown compound that is a metal sulfate hydrate. The general formula for a metal sulfate hydrate (MSH) is $M_x(SO_4)_y \bullet z\, H_2O$. You are asked to determine the identity of the unknown by comparing the % SO_4 and % H_2O in your unknown compound to those for a list of possible compounds.

We will dissolve the metal sulfate hydrate in water and then add a solution of $BaCl_2$. The sulfate ion (SO_4^{2-}) will precipitate with the Ba^{2+} ions to form $BaSO_4$, which precipitates out by gravity (gravimetric) and we will collect the $BaSO_4$ by filtration.

The unknown sample that you will be given is one of the six following metal sulfate hydrates:

$NiSO_4 \bullet 6H_2O$
$Na_2SO_4 \bullet 10H_2O$
$MgSO_4 \bullet 7H_2O$
$MnSO_4 \bullet H_2O$
$KAl(SO_4)_2 \bullet 12H_2O$
$CuSO_4 \bullet 5H_2O$

The various metal sulfate hydrates are similar to one another in that all consist of a metal ion, the polyatomic sulfate ion, and various numbers of "waters of hydration". The waters of hydration are loosely bonded in a particular numerical ratio to the metal sulfate, forming an integral part of the crystal structure. The water can be driven off by heating, leaving behind the anhydrous metal sulfate (MS).

This experiment has three parts:

- Determine the percentage, by mass, of H_2O in the sample.
- Determine the percentage, by mass, of SO_4^{2-} ion in the sample.
- Determine the likely identity of your MSH by matching your experimentally determined values with the various unique values calculated from the different possible molecular formulae of the five possible unknowns.

The method for determining the mass % water is straightforward. Carefully take the mass of a test tube (after driving off the absorbed water), add your compound and take the mass again. Drive off the water by moderate heating and take the mass again. You will collect the following data:

Mass of test tube
Mass of test tube + unknown compound (MSH)
Mass of test tube + compound after heating (now just a MS)

From these data, you can calculate the mass of the unknown compound (MSH), mass of the heated compound (the anhydrous MS), water lost due to heating, and the mass percent water:

$$\text{mass \% } H_2O = \frac{\text{mass of water}}{\text{mass of MSH}} \times 100\%$$

Determining the % SO_4^{2-} is more complex. A carefully weighed sample of the original unknown sample is dissolved in water, allowing the SO_4^{2-} ions to go into solution. All six possible unknowns are soluble in water. An excess of Ba^{2+} ions (in the form of $BaCl_2$) are added to the dissolved metal sulfate. Insoluble $BaSO_4$ is formed and precipitates out of solution as a solid. It is recovered through filtration, dried and weighed.

$$M_x(SO_4)_y \bullet z\, H_2O_{(aq)} + BaCl_{2(aq)} \rightarrow \mathbf{BaSO_{4(s)}} + MCl_{w(aq)}$$

All of the sulfate in the barium sulfate recovered is from the unknown metal sulfate hydrate. Therefore, if we can calculate the mass of sulfate in our precipitate, we know the mass of sulfate from our original sample.

$$\text{mass } SO_4^{2-} = \frac{\text{molar mass } SO_4^{2-}}{\text{molar mass } BaSO_4} \times \text{ mass of } BaSO_4 \text{ recovered}$$

$$\text{mass \% } SO_4^{2-} = \frac{\text{mass } SO_4^{2-}}{\text{mass of MSH}} \times 100\%$$

At this point, compare your % SO_4^{2-} and % H_2O to the list of six possible unknowns and make the best selection possible. If your results are indeterminate, narrow the possibilities, but report all of the most likely identities.

You can also make use of general chemistry reference guides. One is called the "CRC" Handbook (Chemical Rubber Corporation, Handbook of Chemistry and Physics). The other is the Merck Index. The CRC Handbook contains most chemical reference material that you will need for all chemistry classes that you take at Skyline College. You will find the information in a table form in the inorganic chemistry section. The section starts with all the abbreviations used in the table. Then compounds are listed as you name them, cation first, anion second. Look under the cations alphabetically, followed by the anions, alphabetically under the cations. Read the table across the page to get color, crystallography, melting and boiling point, solubilities in cold and hot water. The Merck Index works like a dictionary. The information is in paragraph form. Read through the paragraph to get the needed information. Caution; The wording of the names is different than how you are taught. Iron (III) is listed under ferric. When in doubt, look in the index in the back to find the name and numbered entry.

Practical issues regarding the procedure:

Heating to a constant mass

In the procedure you will be asked to "heat to a constant mass". This is a process to ensure that all of the water adsorbed on surfaces from the atmosphere has been removed. Water from the atmosphere is a problem because it gets weighed in the mass of the test tube or filter paper. It is a source of error. We heat a test tube to drive off this "physically absorbed" water prior to weighing the test tube. The test tube is cooled and weighed. We reheat the test tube, cool and weigh again. We repeat the heat, cool, weigh process until the mass of the test tube remains constant (*i.e.* all the water is driven off). We do the same thing when we measure filter paper with collected precipitate, except we use lower temperatures in an oven (so that the paper is not charred). Note: if a test tube is too hot to hold, it's too hot to weigh!

Precipitation of $BaSO_4$

We will want to add an excess of $BaCl_2$ to the metal sulfate hydrate to ensure that all of the sulfate ion is precipitated. However, we don't know which of the six compounds we have. In order to ensure that you will have enough $BaCl_2$ to fully react the sulfate from any unknown, we will base the volume we use on the MSH with the greatest percent sulfate, which is manganese (II) sulfate monohydrate. We will then add 10% additional barium chloride beyond that value. The excess barium stays in solution, all the sulfate available reacts with the barium ion, forming the precipitate. We make sulfate (from the metal sulfate) the limiting reagent.

You will be working with an acidic solution of the metal sulfate hydrate. This is to minimize a side reaction, as follows: $CO_{2(g)} + H_2O_{(l)} \Leftrightarrow H_2CO_{3(aq)} \Leftrightarrow 2\ H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$

This reaction is reversible, and we can push the equilibrium to the left (toward reactants) by increasing the amount of H^+ ions (acid) present in solution. We wish to do this to prevent the the precipitation of our Ba^{2+} ion as barium carbonate: $CO_3^{2-}{}_{(aq)} + Ba^{2+}{}_{(aq)} \rightarrow BaCO_{3(s)}$

These secondary reactions can occur because CO_2, from the air, readily dissolves in the water. The resulting carbonate ions react with the barium ions, increasing the mass of the precipitate (and causing error).

Barium sulfate is highly insoluble. It precipitates as very fine crystals, some of which will pass through the filter paper used to collect it. We want to use a technique to produce larger crystals that will be trapped by the filter paper. This technique is called "digestion". The mixture containing the precipitated barium sulfate is kept hot, but not boiling, for at least 30 minutes before being allowed to cool. The process of dissolving and re-precipitating is affected by the surface area to volume ratio of the crystals. Small crystals, with a larger surface area to volume ratio redissolve more quickly. Precipitation then occurs on larger crystals. The net result is larger crystals. Solubility is temperature dependent, and digestion occurs much faster at higher temperature. Boiling is not desired as it "stirs up" the precipitate that should be settling on the bottom.

We can test the digested solution to see that all the sulfate has precipitated by adding an additional drop of $BaCl_2$ (once the precipitate is settled and the solution is clear). If a white cloud of new precipitate occurs, unreacted sulfate still remains and you should add another 2-3 mL of $BaCl_2$, reheat and test again. If an additional drop of $BaCl_2$ causes additional new precipitate, you likely need to recalculate the amount of $BaCl_2$ and begin the digestion process again.

EXPERIMENTAL PROCEDURE

Day 1. A. Determination of the water content

1. Obtain an unknown sample and record its number. Be sure to write down observations about your compounds, for example: color, appearance of the crystals, if the compound melts when heating (later in the experiment), and any other notable characteristics.
2. Obtain a Pyrex or Kimex test tube from the stockroom or your tray. Wash and clean the test tube thoroughly.
3. Heat the whole test tube briefly over a Bunsen burner, using a test tube holder. Let the test tube cool. Weigh the test tube, heat again, cool and weigh again (heat to a constant mass). You must repeat the heat/cool/weigh cycle until the mass of the test tube is constant.
4. Carefully place 4-5 grams of unknown compound into the test tube and record the weight, to the nearest 0.001 grams.
5. Use a test tube holder to slowly heat the sample over a Bunsen burner flame. Rapid heating can cause spattering as the water escapes suddenly. Heat the top of the test tube also, to remove condensed moisture.
6. Some of the samples will liquefy. Water is still being driven off. Avoid very intense heating of the liquids, which may cause the compound to decompose. Heat the sample until no additional water is visibly escaping. This may take 10-20 minutes (or longer). Cool, mass the test tube and compound. Repeat the process, heating to a constant mass. Be sure to record each successive mass. For the second and subsequent heatings, about five minutes of heating will usually suffice.
7. Calculate the mass of your anhydrous metal sulfate.
8. Calculate the weight of water driven off.
9. Calculate the mass % water of the MSH.

Day 2 Determination of the Sulfate Content

10. Weigh out, to the nearest 0.0001 gram, a sample of the original unidentified metal sulfate hydrate (about 0.5 to 0.6 g). Carefully transfer the sample to a beaker and add about 150 ml of deionized water. The amount of water is not critical since the amount of SO_4^{2-} ions that will end up in the precipitate will be the same in any case.
11. Add 2-3 drops of Hydrochloric acid to the solution, in order to acidify the solution.
12. The $BaCl_2$ will be made available in the form of a saturated solution, of about 0.28 M. We will want a slight excess of $BaCl_2$ in our solution. After you have shown your instructor the volume of solution calculated, measure it out.
13. Add the barium chloride solution to your beaker of sulfate compound and stir. Be sure to rinse any of the precipitate on the stirring rod back into the beaker with deionized water.
14. Digest the solution for 30 minutes at slightly less than 100°C (about 80-95°C). Boiling will not harm the solution but it prevents the solid from settling out. Once the solution boils, reduce the heat so that the solution "simmers", without boiling. (this allows the solids to settle to the bottom).
15. Once the digestion has started, you have time to label a circle of filter paper with your name (in pencil) and weigh it. Record the mass in your notebook. Weigh the paper to a constant mass, by heating in the oven (at 60-75 deg C.), massing, reheating, and remassing until the mass remains constant (within 0.01 g). Let the paper remain in the oven at least 15 minutes before the first weighing and 10 minutes between later weighings.
16. Let the solution settle and add an additional drop of barium chloride. If a white cloud forms at the point where the drop hits the solution, add another 2-3 mL of $BaCl_2$ solution, heat and test again.
17. If a white cloud still forms, you should check your calculations and consider repeating this analysis again.
18. After the solution has digested and has been tested for complete precipitation, remove from the heat and place on a wire mesh to cool. The solution does not need to cool to room temperature, just enough to allow you to safely work with the solution.
19. Fold and place the weighed filter paper into a funnel. Wet with deionized water.
20. Slowly pour the mixture through the funnel to recover the precipitate. It will go faster if you let most of the clearer solution go through first. Be careful not to allow the mixture to go above the level of the paper in the funnel, or you will lose some of the precipitate around the side of the paper.
21. Use deionized water to rinse the last of the precipitate out of the beaker onto the filter. Wash the precipitate by pouring through two 5-mL aliquots of deionized water.
    a. If your lab period is nearly over, the filtering solution can be placed in a quiet place to continue filtering overnight.
    b. If you have time, complete the procedure under Day 3.

Day 3: Dry and weigh the filter paper.

22. Carefully remove the filter paper from the funnel and place the filter and contents into a beaker. Put this into drying oven at ~ 60°C for at least 40 minutes (or overnight). Check the oven temperature, if it goes much above 60°C, the paper can char.
23. Heat the filter paper + precipitate ($BaSO_4$) to a constant mass. Record each successive mass in your lab notebook (not just the final mass). When two successive masses are essentially identical, you can assume the material is dry.
24. Calculate the mass of the precipitate. Calculate the mass of sulfate in the precipitate.
25. Calculate the mass percent of sulfate in the original sample.

Calculation of the mass of sulfate in your $BaSO_4$ precipitate.

From the mass of your dried precipitate, you can calculate the mass of sulfate using the $\%SO_4^{2-}$ in barium sulfate, which you calculated in prelab question #6. This value is the same regardless of your unknown, as $BaSO_4$ is the precipitate in all cases. The mass of sulfate you calculate is the mass of sulfate that came from your original MSH unknown sample.

RESULTS

Summarize your results for the % sulfate and % water of your unknown. Identify your unknown.

DISCUSSION / ERROR ANALYSIS

1. Which compound is likely your unknown? Briefly discuss how you used your results to make this assignment. If it could be more than one, explain this also.

2. If in doubt about the identity of your unknown, check the properties of the six different compounds in the *Handbook of Chemistry and Physics or Merck Index*. Use color, melting point, and other properties to better define your unknown.

3. Based on your best determination of the identity of your unknown, calculate the percent error for % sulfate and % water of your unknown. Discuss where these errors might have arisen. How might you improve or modify your procedure if you were to do this experiment again?

4. Discuss two good ideas for how to do the lab better, if you were to repeat this experiment.

CONCLUSIONS

In prose (paragraph form), state:

- Percent sulfate of the unknown
- Percent water of the unknown
- Your Unknown # and your assignment of the identity of the unknown (and secondary possibilities if unsure).

Metal Sulfate Hydrate Experiment • Assignment & Report Guidelines

READING Experiment – Lab Manual Pages

Laboratory Handbook:
Section VI - Heating Sources & Techniques
- Please read all subsections.

Section VII - Separations Introduction
- "Decantation"
- "Filtration"

Chemistry, 5th ed. by Silberberg: pp. 69, 72, & 96 – *read the subsection starting on each page.*

PRE-LAB Begin the prelab on a new page of your laboratory notebook. **ALL elements of the pre-lab MUST be completed before an experiment is started.** The COPY page from your notebook will be collected as you enter the lab. The original pages must stay in your notebook.

Prelab – Day 1

Heading
- Title of the experiment, your name, the date.

Purpose
- Briefly, but specifically explain the purpose of the experiment. Be sure to specifically state the two quantities you will determine and what you will use them to accomplish.

General Strategy (for the determination of the percent water in the MSH))
- **Summarize** the procedure of this part of the experiment, and **explain** how you will use the data you measure to determine the quantities you want to find, and the identity of the unknown. Showing the important equations needed in calculation can be helpful.

Known MSH Summary Table
- Copy and complete the following table into your lab notebook on a page that gets turned in as part of the prelab. Show your calculations in your lab notebook for at least one of the compounds not done as an example in class. Express all answers to the correct number of significant digits.

Metal sulfate hydrate	Compound name	Molar mass	% H_2O by mass	% SO_4^{2-} by mass
$NiSO_4 \cdot 6H_2O$				
$Na_2SO_4 \cdot 10H_2O$				
$MgSO_4 \cdot 7H_2O$	Complete in your LAB NOTEBOOK			
$MnSO_4 \cdot H_2O$				
$KAl(SO_4)_2 \cdot 12H_2O$				
$CuSO_4 \cdot 5H_2O$				

Continued on the next page.

Data Table

- Read through the procedure and determine what information you will need to put into the data table. Set up this data table in your lab notebook.

Answers to Pre-Lab Questions #1 and #2.

Prelab – Day 2

Heading

- Title of the experiment, your name, the date.

General Strategy (for the determination of the percent sulfate in the MSH)

- **Summarize** the procedure of this part of the experiment, and **explain** how you will use the data you measure to determine the quantities you want to find, and the identity of the unknown. Showing the important equations needed in calculation can be helpful.

Calculation of the volume of $BaCl_2$ solution required.

- The following method will help you calculate a volume of solution that will include an excess of $BaCl_2$ to ensure complete precipitation of the sulfate ion in your unknown as barium sulfate. ***Note***: regardless of your unknown, free sulfate ions are produced when you dissolve it.

- Assume that you will start with 0.600 grams of MSH sample. Also assume that you have the unknown with the largest $\%SO_4$, $MnSO_4 \bullet H_2O$, and calculate the mass of sulfate ion in your 0.600-g sample.

- Using dimensional analysis, determine the quantity of barium chloride solution needed to fully react with all of the sulfate ion.

  The solution of $BaCl_2$ that we will use is saturated with $[BaCl_2] = 0.28\ M$. Barium chloride dissociates into water as follows:

  $$BaCl_{2(aq)} \rightarrow Ba^{2+} + 2\ Cl^{-}$$

  You get one barium ion for each formula unit. Therefore, $[Ba^{2+}] = 0.28\ M$ as well. The Ba^{2+} reacts on a one-to-one ratio with sulfate:

  $$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_{4(s)}$$

  Multiply the volume of solution required by 110% (1.10) to ensure that you have an excess of Ba^{2+} ions. Show this result to your instructor prior to pouring it into the solution containing the metal sulfate. Write the volume needed in your lab book.

Data Table

- Read through the procedure and determine what information you will need to put into the data table. Set up this data table in your lab notebook.

Answers to Pre-Lab Questions #3 and #4.

LAB REPORT *Begin the lab report section on a new page of the lab notebook.* ***The discussion and conclusion sections should be word-processed.*** Other parts of the report - calculations, etc. may be typed or written in the lab notebook.

Heading

- Title of the experiment, your name, the dates the experiment was performed.

Data / Observations / Results

- ORIGINAL QUANTITATIVE DATA (signed data pages from your lab notebook).
- Qualitative data (observations) –describe the unknown appearance in your lab notebook. It may help in identification. Also make observations about the solutions, the heating process for dehydration, the appearance of the dehydrated product, *etc*.

Calculations

- Show calculations for the following quantities in your report (use proper format for labeling and showing calculations in a formal report):
  - Percent of water in your metal sulfate hydrate.
  - Volume of $BaCl_2$ solution to use for your sample.
  - Percent of sulfate in your metal sulfate hydrate (there are multiple steps in the calculation process).

Discussion – Theory / Results / Error Analysis

In this section, you will explain the experiment, evaluate and discuss your results, and analyze error. ***This section REPLACES the Discussion questions in the lab manual.***

- Conceptually explain the experimental process for the determination of the percent water in your unknown.
- Conceptually explain the experimental process for the determination of the percent sulfate in your unknown.
- Summarize the unknown number, % water, % sulfate, physical appearance, and other observations about your unknown. (*e.g.* melted on heating, *etc*.)
- Find physical data about your likely unknown – the CRC *Handbook of Chemistry & Physics* is a good source of information.
- Identify your sample based on the above criteria. If it could be more than one possibility, explain this also.
- Based on your determination of the identity of your unknown, calculate the percent error for % water and % sulfate in your unknown.
- Separately discuss where error might have arisen in the % water and % sulfate experimental determinations. Be specific with regard to your experimental value being too high or too low.
- Suggest modifications you could make to the procedure to improve your results.

Conclusions

- In prose (paragraph form), state your unknown number, percent sulfate of the unknown, percent water of the unknown and your assignment of the identity of the unknown (and secondary possibilities if unsure).

Metal Sulfate Hydrate **Name:** ________________________

PRELAB QUESTIONS

1. What is the mass percent of sulfate in $BaSO_4$?

2. When you dry or dehydrate a sample, how do you know that the process is complete?

3. A student added an insufficient amount of $BaCl_2$ to the solution of the metal sulfate. Would the final calculated percentage of sulfate be too high or too low? **Explain why.**

4. If some of the barium sulfate crystals pass through the filter, consider what you might do to salvage the situation?