Question

- How pure is my sample of malachite and is it cost effective to make this for my roommate?

Skills

- Pipette standards and prepare a standard absorption curve with an R^2 value greater than or equal to 0.98.
- Use the standard curve to determine the percent copper in your malachite sample.
- Estimate the purity of your product, based on the percent copper, and evaluate the cost to synthesize the malachite for your roommate.

Introduction

In the previous lab, you synthesized malachite—at least we assumed this was the final product. In reality, your product is likely a mix of malachite, $Cu_2(OH)_2CO_3$, and copper(II) carbonate, $CuCO_3$. It is also possible that there is a little copper(II) hydroxide, $Cu(OH)_2$ or copper(II) oxide, CuO in your sample. The percent of copper in copper(II) carbonate, copper(II) hydroxide, and copper(II) oxide differs from that of malachite. You will analyze the amount of copper in your sample with a spectrophotometer (similar to the analysis of Himalayan pink salt) and determine the purity of your synthesis product.

Assume that a student determined that their malachite sample was 59.53% copper by mass. Malachite is only 57.48% copper by mass (see Table 1). Their product must also contain a material that has a higher percent copper, or copper(II) oxide, 79.89% copper by mass.

Table 1: Summary of Percent Copper in Copper-containing Compounds

Compound	Percent Copper by Mass
Copper(II) carbonate	51.43
Malachite	57.48
Copper(II) oxide	79.89

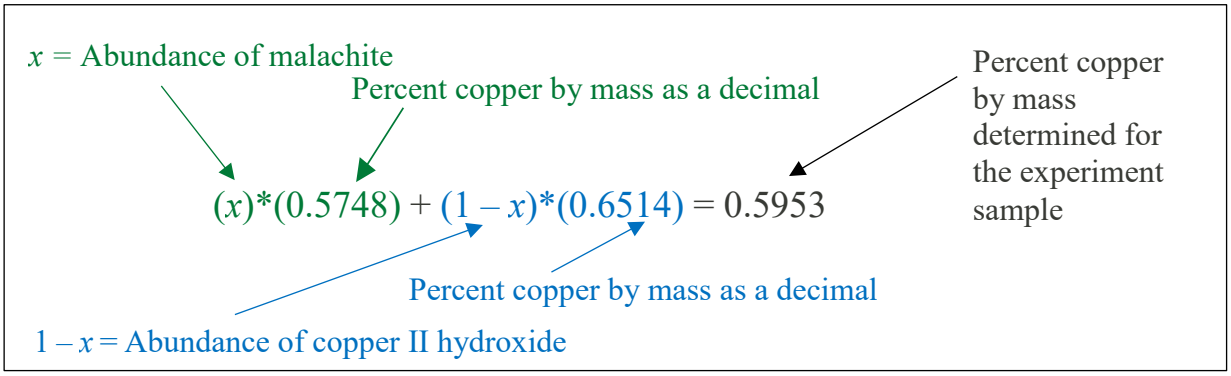
To determine the percent of malachite in this student's product, assume that their product contains only malachite and copper(II) oxide. The product is more malachite than copper(II) oxide, since 59.53% is closer to 57.48% (malachite) than 79.89% (copper(II) oxide). Taking the average of the percent values gives 68.69%, so simply taking the average gives an incorrect answer. The malachite and copper(II) oxide are not present in equal amounts, so a **weighted average** must be

calculated. This calculation is how the average atomic masses of elements are calculated from the percent abundance of isotopes, you may have seen or done this calculation in the first few weeks of lecture.

It is easiest to work with each percent written as a decimal in this calculation. Let x = abundance of malachite and 0.5748 its percent copper by mass (decimal form).
Let (1-x) = abundance of copper(II) oxide and 0.7989 its percent copper by mass.

The abundance times the percent as a decimal for each material, added together, equals the percent copper in the product, again written as a decimal.

Solving for "x" gives the percent abundance of malachite in the product. Here, x = 0.9045. In other words, the student's product is 94.45% malachite.



In the lab ***Analysis of Table Salt***, you prepared several standards of iron (methyl orange standards) and used an absorbance spectrometer to make a standard curve. You measured the absorbance of the iron from your salt samples and determined the concentration of iron in your salt. You will use a similar procedure in this lab.

You will prepare a standard curve of solutions containing different concentrations of bromocresol green adjusted to match color of the copper amine complex ion in the sample. This is the mastery component of this experiment—pipetting standards and preparing a standard curve. After you have accomplished these tasks and have an acceptable regression line, you will analyze your malachite sample to determine the concentration of copper(II) ion in a solution of your sample. From the molar concentration of copper(II) ions in your sample, you can determine the percent of copper by mass in your sample and calculate the actual cost of synthesizing malachite for your roommate.

Copper solutions in the form we are analyzing can be toxic to plant and aquatic life; therefore, solutions made from malachite cannot go down the drain. The standard stock solution has been prepared from a common acid-base indicator that it is not toxic to plant and aquatic life, so all solutions made from the standard stock solution can go down the drain.

References

Brigandi, L. M.; Leber, P. A., and Yoder, C. H. "Synthesis and Analysis of Copper Hydroxy Double Salts", *J. Chem. Educ.*, Vol. 82, No. 11: 1662.

Acknowledgements

Benjamin Thome (GVSU student), Mary Jo Smith, and Julie Henderleiter adapted the procedure for this lab from the article by Brigandi, Leber, and Yoder.

Equipment and Materials

0.0315 M Bromocresol green stock solution		Pipette bulb
2.0 M HNO_3, dropper bottle	50 mL beaker	Spatula
2.0 M NH_3, dropper bottle	5 large test tubes	Plastic weigh boat
Vernier SpectroVis Plus	5 stoppers for lg. test tubes	Small funnel
Volumetric pipettes	Test tube rack	Wax pencil or Sharpie ™
10.00 mL volumetric flask	1 cuvette	Glass stir rod

Experiment Procedure

Part A is completed with your partner. Parts B, C and D must be completed individually.

2 M nitric acid (HNO_3) may be corrosive to metals, can cause skin burns and damage to eyes. You will be using drops of this but still use caution. Be careful not get it on your skin or belongings and do not breathe in the vapors from the bottle. Keep the bottle closed when not in use.

2 M aqueous ammonia (NH_3) causes skin irritation and can cause eye damage. You will be using drops but still use caution. Be careful not to get it on your skin or belongings, and do not breathe in the vapors from the bottle. Keep the bottle closed when not in use.

Part A: Dissolve the Malachite Sample

1. Obtain the malachite you synthesized in the previous lab. Take the mass of the vial, cap and product. Check this mass against the mass you recorded last week. You can go back and view last week's data in Labflow. If the masses are different then your product may have been wet at the end of that lab.
2. Use a stir rod gently to break up the malachite into a powder inside the vial. Smaller particles will dissolve faster, powdered is best.
3. Accurately weigh between 0.100 – 0.125 g of your malachite into a 'large-mouth' 10.00 mL volumetric flask. If you don't have 0.150 grams see your instructor for additional malachite.

   What is the actual mass of malachite used in the volumetric flask, in grams? _____

Note: If the opening of the volumetric flask is not wide enough to weigh directly into the flask, use a weigh boat and transfer the sample into the 10.00 mL volumetric flask using a small funnel and several drops of 2.0 M nitric acid, HNO_3, to rinse the malachite into the flask.

4. Add 25 drops of 2.0 M HNO_3 dropwise into the volumetric flask containing the malachite. Swirl gently for up to five minutes. Fizzing will occur, as carbonates and the acid form carbon dioxide gas.
5. If the sample is not dissolved after mixing for 5 minutes, add 2-6 more drops of 2.0 M HNO_3, and swirl to dissolve/mix. If the sample does not dissolve within the next 5 minutes, consult your lab instructor.
6. Be sure your solution is not cloudy at all before moving on to the next step.
7. Add 60 drops of 2.0 M ammonia, NH_3, *DROPWISE* to the solution while swirling the flask until the solution turns a deep purple-blue and there is no solid present. A light blue solid will form as the ammonia is first added, this solid will dissolve as more ammonia is added. If the solid, any cloudiness or haziness is still present, consult your instructor.
8. Once the solid has completely reacted with the ammonia, add 5 more drops of 2.0 M ammonia.
9. When the solid is completely dissolved, fill the flask to the mark with deionized water.
10. Cap the flask and hold the cap on as you invert the flask to mix the solution. Invert the flask 2-3 times, and then loosen the cap to vent the gas. Repeat 4-5 times to ensure thorough mixing.

    TAKE CARE, when inverting the flask to mix! Some dissolved CO_2 will come out of solution and may pop/loosen the cap of the flask.

11. Transfer the solution to a clean, dry, labeled test tube and cap the test tube to minimize evaporation of NH_3. This copper solution contains copper as the deep blue-purple $Cu(NH_3)_4^{2+}$ ion. The solution is too concentrated and needs to be diluted further before it can be analyzed.
12. Wash and DI rinse the volumetric flask.

Part B: Dilute Malachite Solution for Absorbance Measurement

1. With a 1.00 mL volumetric pipette, transfer 1.00 mL of the dissolved malachite solution, now a copper amine complex ion, prepared above, into a clean 10.00 mL volumetric flask.
2. Add 25 drops of 2.0 M NH_3 to the volumetric flask.
3. Dilute the sample to the 10.00 mL volume mark with deionized water. If any cloudiness develops as you add DI water, stop adding water and notify your instructor.
4. Hold the cap on the flask and invert to mix well.

5. Transfer the solution to a dry, labeled test tube and place the stopper in it. This is the malachite solution of which you will measure absorbance in Part D Wash your volumetric flask and rinse it with deionized water.

Part C: Preparation of Standards

1. In the Pre-Lab, you calculated the volume of 0.0315 M Bromocresol green standard stock solution needed to make 10.00 mL of 3 dilute standards, (Standard 3) 0.0189 M HBcg, (Standard 2) 0.0126 M HBcg, and (Standard 1) 0.00630 M HBcg. You will now make these solutions.
2. The concentration of the standard stock solution has been adjusted to compensate for the 1.00 mL to 10.00 mL dilution of the original malachite sample.
3. Obtain about 30 mL of the 0.0315 M HBcg standard stock solution in a beaker. Each person must make each standard. Recall that you should never pipet out of a stock bottle.
4. Use the stock solution to prepare each of the standards. Begin by preparing the standard with the smallest concentration, working toward the standard with the highest concentration. This will lessen the likelihood of contamination from a less-than-clean volumetric pipette or volumetric flask.
5. After making each standard, transfer it to a labeled, large test tube and place a stopper in the test tube.
6. Wash your volumetric flask and rinse with DI water after making each solution.

Part D: Analysis of Standards and Unknown

1. Each person will calibrate the Vernier SpectroVis Plus, measure their standards and malachite solution and create a standard absorption curve for their data individually.
2. Use the Logger Pro program on a laptop computer in the lab and a Vernier SpectroVis Plus spectrometer to measure the absorbance of each standard.
3. Follow the instructions in Appendix E, Part A to set up and calibrate the spectrometer. Set the spectrometer to measure at a wavelength of 612 nanometers. Use deionized water as your blank.
   What is the actual wavelength your spectrometer is set to? _____
4. Continue to refer to the instructions in Appendix E, Part A. Measure and record the absorbance of the deionized water blank. Use a small amount of each standard solution to rinse the cuvette before filling it three quarters to measure the absorbance. Discard the solutions in the sink after measuring each. Measure each standard from the lowest to highest concentration and record the absorbance.
5. Next measure and record the absorbance of your dilute malachite sample. Return the sample to the test tube after measuring. DO NOT discard.

6. Use a computer that has Excel® downloaded on it to plot absorbance versus concentration for the standards and the water blank on Excel®. See Appendix D for instructions using
   Excel® to graph. As you have done in previous labs, add a trendline, the line equation and R^2 value to the graph. Refer to Appendix C to make sure you have included all the required criteria for a good graph.
7. Have your instructor review your graph to determine if it is acceptable. If it is not acceptable, do the following:
   a. Your instructor will help you determine which standards should be re-made.
   b. Remake the standards that were suspected to be out of linear alignment.
8. Re-measure the absorbance of the blank, each standard and your product until your curve is appropriately linear.
9. You can click "Back" to go back and change any of the absorbances needed before continuing on to the calculations.
10. Once the graph is acceptable, save it. You will upload a picture or PDF of it in your lab report.

Clean up

1. Dispose of the materials as follows:
   a. Pour all copper waste (solution(s) made from malachite samples and contaminated solid malachite - brown or black product) into the labeled copper waste container in the fume hood.
   b. Recall that the Bromocresol green standards can go in the sink with water.
   c. If your percentage copper is acceptable (check with your instructor), place any leftover solid malachite in the container labeled for solid malachite.
   d. **Remove the tape from the shell vial.** Rinse out any residual malachite from the vial using 1M nitric acid. The nitric acid, 1 M HNO_3, is in a dropper bottle in the hood next to the copper waste container. Put the nitric acid rinse into the copper waste container. **Place the cap and vial into the collection bin separately.**
2. Use hot soapy water to wash all glassware and appropriate equipment. Rinse well with hot tap water.
3. DI rinse all washed glassware and equipment then return to the place you obtained it. Let air dry.
4. Fill the DI water bottle that is at your lab bench.
5. Check the list on the end of the bin and make sure all of the items are in the bin. If materials are missing let your instructor know so that they can be replaced.

6. Clean the common area assigned to you by your instructor.
7. Clean the balance with the brush as needed. Use the disinfectant sprayed onto a paper towel to wipe the touch pad and guard/doors on the balance.
8. Return your personal items to your pack/bag.
9. Disinfect your work area(s) that cannot be washed in the sink with disinfectant spray. DO NOT wipe – Let disinfectant air dry.
10. Wash your hands before you leave the lab.