Chemistry 105
The Chemistry of Color
Laboratory Meeting 4

Agenda

- Introduction to Today's Lab
- *Experiment: Synthesis of Several Pigments*
- *Experiment: Making a Small Fresco*
- *Experiment: Synthesis of Several Pigments*
- Data Analysis, Post Lab Questions and Homework Help

Synthesis of Several Pigments

The lab will be set up so that there is one station for each pigment. Please choose an open station and rotate through all of the pigments. Usually, two groups can work at a station at once. If the stations for the pigment or pigments you have left are all full, take a break and make your fresco.

A: Synthesis of Zinc Chrome Yellow "School Bus Yellow"

Chrome yellow is a pigment first extracted Louis Nicholas Vauquelin from the mineral chrocoite around 1800. Its chemical formula is $PbCrO_4$. By the 1820's it and other "chromate pigments" were in wide use. Use of these pigments continues today. Chromate pigments contain the ion *chromate*, with formula CrO_4^{2-}. Unfortunately, chrome yellow contains lead, a toxic heavy metal.

Zinc chrome yellow is an alternative yellow pigment that does not contain lead. It is formally basic zinc chromate, $ZnCrO_4 \bullet Zn(OH)_2$. We will make this pigment first by mixing potassium chromate K_2CrO_4 and zinc chloride $ZnCl_2$, and then adding NaOH to make the solution basic. The result is solid yellow $ZnCrO_4 \bullet Zn(OH)_2$.

Directions:

1. Pour 5 mL of a 0.5 M solution of sodium or potassium chromate (Na_2CrO_4 or K_2CrO_4) into a beaker. Record the color of the solution below.

   Color of solution:

2. Add 5 mL of a 0.5 M solution of zinc sulfate or zinc chloride ($ZnSO_4$ or $ZnCl_2$) to the beaker and stir the two solutions together. Describe exactly what happened below when the two solutions were mixed together.

3. Add about 1.5 mL of 6 M NaOH to make the solution basic. Stir well. Describe any changes in the appearance of the solution.

4. Filter the precipitate (the solid formed) which is basic zinc chromate ($ZnCrO_4 \bullet Zn(OH)_2$) using gravity filtration. Allow the pigment to dry uncovered on the filter paper in the designated area.

The first step in this synthesis is an example of a **Double Replacement Reaction**. In such reactions, the positive ions in two reacting ionic compounds switch partners.

Examples:

$$BaCl_2 + K_2SO_4 \longrightarrow 2\ KCl + BaSO_4$$

$$FeCl_3 + 3\ NaOH \longrightarrow Fe(OH)_3 + 3\ NaCl$$

Below is the partial chemical equation for the first step in the synthesis. Following the examples above, predict the other product formed in this reaction and balance the resulting equation:

$$Na_2CrO_4 \quad + \quad ZnSO_4 \quad \longrightarrow \quad ZnCrO_4 \quad + \quad \underline{\hspace{3cm}}$$

B: Synthesis of Synthetic Malachite

The pigment malachite is formed by grinding and washing the familiar green banded mineral. It was used in Egyptian tomb paintings and was popular in Europe in the 15th and 16th centuries. The formula of malachite is basic copper carbonate, $CuCO_3 \bullet Cu(OH)_2$.

Here, we make a synthetic alternative preparation from copper (II) sulfate and baking soda.

$$2CuSO_4 + 4NaHCO_3 \longrightarrow CuCO_3 \bullet Cu(OH)_2 + 2Na_2SO_4 + 3CO_2 + H_2O$$

1. Measure out 5 mL of a 0.5 M solution of copper sulfate ($CuSO_4 \bullet 5\ H_2O$) into a 50 or 100 mL beaker.
2. Add up to about 3.0 g of solid sodium bicarbonate ($NaHCO_3$), a little at a time with stirring, until all the fizzing has stopped and the reaction is complete.

   Describe what happens:

3. Using gravity filtration to filter the precipitate of basic copper carbonate $CuCO_3 \bullet Cu(OH)_2$ that has formed.
4. Allow the pigment to dry uncovered on the filter paper in the designated area.

C: Synthesis of Chromium Oxide Green "Army Green"

From: Hill, P.S. "Chemistry and Art" Millersville University, 2005.

Chromium oxide green was first identified in 1780 and is used as a commercial pigment in camouflage coloring, ceramics, enamels and a variety of other applications today. We will start with sodium dichromate, $Na_2Cr_2O_7$ and form the pigment Cr_2O_3.

1. Weigh out 3.0± 0.1 g of sodium dichromate in a weighing boat. Record the mass here:

2. Weigh out 0.45± 0.01 g of sulfur in a weighing boat. Record the mass here:

3. Empty contents of both cups into a mortar and grind it very finely using the pestle
4. Transfer the finely ground mixture into a porcelain crucible by tapping gently on the weighing boat and sliding the powder into the crucible.
5. Place the crucible in a wire triangle on a ring stand. Set up a Bunsen burner so that the crucible bottom is 1.5 inches above the top of the burner. THIS SHOULD BE DONE IN THE FUME HOOD.
6. Heat the contents of the crucible with the burner and observe what happens (Record below).
7. When no more gas is given off, the reaction has ceased and and you can turn off the burner and let the crucible cool
8. Loosen the solid from the crucible using a spatula and return the solid to a clean, dry mortar and grind the solid with the pestle.
9. Transfer the powder to a 150 mL beaker and wash the mortar with distilled water, transferring the washings to the beaker.
10. Fill the beaker half full with distilled water and stir vigorously to dissolve any unreacted starting materials. The chromium oxide green pigment will be insoluble.
11. Filter the pigment out of the mixture using vacuum filtration and a Büchner funnel (consult instructor/TA for help). Rinse with acetone to dry the sample.
12. Transfer the chromium oxide green to a weighing paper and weigh it on the balance. Record the mass here:

record your observations:

The Making of a Small Fresco

Make a fresco! (These directions are available in a separate handout in the lab.)

Test the pH of the lime plaster using the pH paper available. pH = ______________

Identify any pigments that were unstable in lime and record them here:

Testing of Pigments and Binders

Here, we will investigate a few of the chemical properties of some of the pigments we made.

Synthetic Malachite

- Test with HCL solution:
  - Obtain a small well-plate. In one of the wells, place a small amount of your malachite pigment.
  - Add about a few drops of the HCl solution to the powder and observe what happens
  - Also, test the pH of the HCl solution. Is this an acid or a base?
- Test with NaOH solution:
  - In one of the wells of the well plate, place a small amount of your malachite pigment.
  - Add about a few drops of the HOT NaOH solution to the powder and observe what happens.
  - Repeat the above two steps with cool NaOH solution and observe what happens.
  - Also, test the pH of either of the NaOH solutions (they are the same, except for the concentration). Is this an acid or a base?

Substance Added	pH acid or base?	Observations During Reaction	Describe Color Change (if noted)
HCl			
NaOH (hot)			
NaOH (cool)			

Prussian Blue

Repeat the HCl and NaOH (cool) tests with Prussian blue.

Substance Added	pH acid or base?	Observations During Reaction	Describe Color Change (if noted)
HCl			
NaOH (cool)			

Paint Binders

There are a number of binders available in the laboratory. Choose two of your pigments to explore with at least two different binders.

- Obtain a white piece of paper and divide it into 4 sections.
- Place a small amount of pigment on a watch glass and add a few drops of the binder of choice.
- Mix well with a spatula until completely blended.
- Paint a sample onto a section of the white paper, labeling the paper with pigment and binder.
- Repeat for a total of at least two pigments in two different binders.

Record your observations:

Questions

1. Transfer your completed equation from the zinc chrome yellow synthesis here:

   Na_2CrO_4 + $ZnSO_4$ $\longrightarrow$ $ZnCrO_4$ + ___________

2. The lead based pigment chrome yellow can be prepared via a double replacement reaction. See if you can predict the products in the equation below and balance the resulting equation.

   $Pb(NO_3)_2$ + K_2CrO_4 $\longrightarrow$ ___________ + ___________

3. The color of pigments can be varied by changing the particle size. Compare the color of your synthetic malachite (very small particles) to the color of the mineral malachite (composed of large particles). Do you think size is a factor?

4. Chromium oxide green, Cr_2O_3 is prepared from $Na_2Cr_2O_7$ through a process known as an oxidation/reduction reaction. Reduction is the addition of electrons to a species, whereas oxidation is the loss of electrons from a species. This can be summarized in the mnemonic **leo the lion says ger**. Leo = lose electron oxidation, Ger = gain electrons reduction. Oxidation and reduction always happen in conjunction, as electrons move from one species (oxidation) to another (reduction).

   Using the following rules, determine the charges on the chromium ions in Cr_2O_3 and $Na_2Cr_2O_7$.

   A few rules for determining the charge on transition metals. The charge is also called the metal's **oxidation state**:

   - Oxygen, sulfur and other elements in the same column (chalcogens) are considered to have a 2- charge
   - Lithium, sodium, potassium and other elements in the same column (alkali metals) are considered to have a 1+ charge
   - Calcium, magnesium and other elements in the same column (alkaline earth metals) are considered to have a 2+ charge
   - Charges on transition metals are determined by determining the charges on the main group elements and the alkali and alkaline earth metals, and adjusting the charge on the transition metal to balance out the overall charge of the substance

   Fill in the following table:

Substance	Total Charge from Oxygens	Total Charge from Sodiums	Total Charge for All Cr's	Charge per Cr atom
$Na_2Cr_2O_7$				
Cr_2O_3				

   Is the chromium ion oxidized or reduced?

5. We've learned about molar masses in this week's discussion. Determine the molar masses of Cr_2O_3 and $Na_2Cr_2O_7$.

6. Determine the number of moles of $Na_2Cr_2O_7$ you used in the synthesis of army green using the molar mass above.

7. Determine the number of moles of Cr_2O_3 you obtained.

8. Determine the % yield of the army green reaction.

9. What is the pH of the lime plaster used in the fresco? Is this acidic or basic?

10. The formula of slaked lime is $Ca(OH)_2$. Justify the answer you gave above in terms of the chemical formula.

11. Which pigments were unstable in the lime plaster?

12. What did you discover about the stability of Prussian Blue and Malachite in different environments?

13. Would you expect Prussian Blue to be stable in Frescoes? Why or why not?

14. How would malachite be affected by acid rain?

15. What did you notice about your pigments in different binders?