Inorganic Pigment Syntheses
PART 1

Many inorganic pigments are prepared by the mixing of two colorless or lightly colored solutions of inorganic chemicals to produce a highly colored, insoluble precipitate of the desired pigment. In this part of the experiment four pigments are produced through precipitation reactions. Observing the precipitation reactions both microscopically and macroscopically can help you better understand what is taking place when the two solutions come together.

Part I. Macroscopic Inorganic Pigment Syntheses

Write balanced chemical equations for the following syntheses. Record all observations.

A. Barium White — An Inexpensive White Pigment

1. Pour 5 mL of a saturated solution of sodium sulfate into a test tube. Record the color of the solution
2. Add 5 mL of a saturated solution of barium chloride to the test tube and mix well. Describe exactly what happened when you mixed the two solutions together.
3. The precipitate formed is very fine and difficult to filter, so you will use centrifugation to separate the solid white pigment, barium sulfate from the excess liquid. Divide your white suspension evenly into two small tubes and centrifuge for 3-5 minutes.
4. Decant the clear liquid. Recover the white precipitate from the test tube and put it onto a small square of filter paper to dry on your bench

B. Chrome Yellow — "School Bus Yellow"

1. Pour 5 mL of a 0.5 M solution of sodium or potassium chromate into a beaker. Record the color of the solution in your notebook.
2. Add 5 mL of a 0.5 M solution of zinc sulfate or zinc chloride to the beaker and stir the two solutions together. Describe your observations when the two solutions were mixed together.
3. Test the pH with either pH or litmus paper. Add 6 M NaOH drop wise to make the solution basic and mix well. The color will change from yellow-orange to bright yellow.
4. Gravity filter the precipitate of zinc chromate.
5. Allow the pigment to dry uncovered on the filter paper on your bench until next week.

C. Synthetic Malachite (Basic Copper Carbonate)

1. Measure out 5 mL of a 0.5 M solution of copper sulfate ($CuSO_4 \cdot 5\ H_2O$) into a small beaker.
2. Add 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.
3. Filter the precipitate of basic copper carbonate —$CuCO_3 \cdot Cu(OH)_2$ — that has formed.
4. Allow the pigment to dry uncovered on the filter paper on your bench until next week.

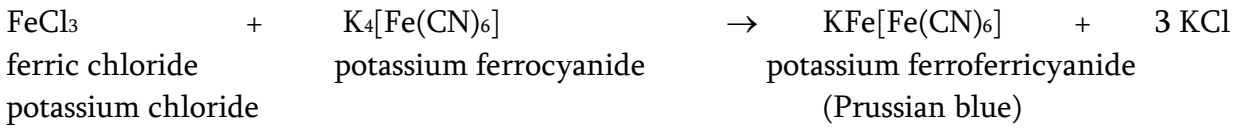
D. Chromium Oxide Green

1. Weigh 3.0 ± 0.1g sodium dichromate and 0.45 ± 0.1g sulfur.
2. Grind both solids together using a mortar and pestle until the powder is very fine and well mixed.
3. Transfer the finely ground mixture into a porcelain crucible using weigh paper.
4. Set up a Bunsen burner, ring stand, and wire triangle in the hood. Place the filled crucible in a wire triangle and adjust so that the crucible in about 1.5 inches above the top of the burner.
5. Heat the contents with the burner until no more gas is evolved. Allow the crucible to cool.
6. Transfer the cooled solid to a second clean mortar and grind with the pestle until fine.
7. Transfer the powder to a 150 mL beaker, using water to transfer from the mortar.
8. Add ~70 mL water and stir vigorously to remove unreacted starting material.
9. Filter the remaining green solid by vacuum filtration. Rinse the pigment with acetone to dry.
10. Determine the final yield.

Part II. A Microscopic Synthesis of Prussian Blue

Each student should perform this synthesis individually.

1. Obtain a clean microscope slide.
2. Place a small drop of 0.5 M solution of iron (III) chloride onto the slide.
3. Place a drop of a 0.25 M solution of potassium ferrocyanide beside but not touching the first drop. Record observations of the solution colors
4. Place the slide on the microscope stage and focus on the first drop.
5. While observing the drop, use a small spatula to drag a small amount of the second drop into the edge of the first.
6. Record your observations when the two solutions were mixed.



Discussion Questions

Calculate your percent yields for all reactions. Offer an explanation for the yields you observed. Compare the microscopic and macroscopic reactions. Which was easier to observe and interpret what was happening as the chemicals mixed?

Inorganic Pigment Qualitative Analysis
PART 2

- ❑ Complete any remaining syntheses from last week.
- ❑ Weigh dry pigments and calculate percent yield.
- ❑ If time allows, observe all dry pigments under the microscope
- ❑ Complete Part III.

PART III: Analysis of Pigments

Art and artifact conservation relies upon analytical chemistry's ability to discover what an object is made of in order to be able to design a proper treatment and conservation plan for the object. Today, conservation artists and scientists are often interested in the determination of authenticity of a painting, understanding the techniques used by the "old masters", and determining the appropriate restoration or conservation treatment for a painting. These issues raise the following questions:

- What pigment did the painter use?
- Is there colored resin or varnish on top of the paint layer causing subtle alterations in the colors we perceive?
- Are we seeing the original color, or has the coloring material gone through alterations with time that have changed its appearance?

Identification of the pigments used in a painting can help us answer some of these questions and address the issues facing conservationists. Fortunately, pigment particles can be characterized by a number of physical properties as well as chemical behavior.

1. Color
2. Size and shape
3. Refractive index
4. Behavior under ultraviolet and/or polarized light
5. Reactivity with other chemicals

In order to carry out an appropriate conservation or restoration plan on a painting or painted object, it is first necessary to understand the composition of the paint. This means determining what type of binding agent was used in the paint preparation and identifying the pigments used as colorants. Pigment identification is also extremely important in painting authentication and dating because the presence of modern pigments such as titanium dioxide (TiO_2) which was not introduced until the 1920's will immediately preclude claims of the painting being from earlier epochs. Pigments can usually be identified by a series of chemical and physical analyses. These analyses involve carefully looking at the pigment both macroscopically and microscopically, carrying out microchemical tests upon a sample of the pigment, and in some cases conducting various types of instrumental analysis on the pigment. However, most identification can be

confirmed with microscopic viewing and a few selected chemical tests. In this part of today's lab you will design an experiment to determine the identity of 5 white pigments and fillers.

Identity of Known Pigments

Chalk or whiting	$CaCO_3$
Lead White	$2\ PbCO_3 \cdot Pb(OH)_2$
Zinc White	ZnO
Gypsum	$CaSO_4$
Titanium White	TiO_2

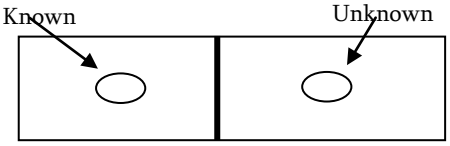
You will have known samples of all 5 pigments and you will have 1 unknown sample that is one of the five. The following reagents will be available to use in testing the pigments.

Reagents

3M HNO_3	KI crystals
3M HCl	10% H_2SO_4

Use the following information to help you in designing your experiment and identifying your unknown.

a. Carbonates will dissolve with effervescence (bubbling) in acids.
b. Lead ion (Pb^{2+}_{aq}) will form a yellow precipitate of PbI if mixed with KI.
c. Titanium white is an extremely inert pigment.
d. $CaSO_4$ will gradually form scattered acicular (needle-like) crystals upon standing in a dilute solution of nitric or hydrochloric acid.



One method for carrying out chemical spot tests is to place small samples to be tested on a microscope slide. Then you can add various solvents and reagents to the sample and observe it carefully under magnification. Once you have tested and observed all known substances, then you can carry out the same tests on your unknown sample. To confirm the unknown's identity it is good to repeat the tests on the unknown and the suspected known on the same slide so you can more closely compare the results.

Pre-lab

Plan out your procedure and design a flow-chart to determine the identity of your unknown. Keep in mind you can observe both chemical and physical properties of the pigments.

Waste Disposal

Collect all unknown waste and discard in provided container.

Discussion Questions

Write balanced equations for all reactions. Were any results surprising? Describe the process by which you came to identify your unknown sample.

References

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