DNAZone Classroom Kit Teacher Guide

Kit title	Chemistry of Color: Pigments In Art
Appropriate grade level	Upper high school, AP Chemistry
Abstract	Students synthesize pigments that have been used in paintings for centuries, opening up an enlightening connection to society and science. Balancing chemical equations and learning about coordinated compounds can be done with the transition metal reactions of these simple syntheses. The naming schemes for compounds based on charged states can be introduced as well. The relationship between subtractive and additive color mixing is also presented to introduce concepts of spectrophotometry.
Time	Most activities in this kit are 2-day experiments of 20-minute sections each day.
PA Department of Education Standards	**Science** • **3.4.12.A.1** Apply rules of systematic nomenclature and formula writing to chemical substances • **3.4.12.A.5** Characterize and identify important classes of compounds (e.g., acids, bases, salts) • **3.4.12.B.3** Use knowledge of oxidation and reduction to balance complex reactions • **3.4.10A:** Explain concepts about the nature/properties of matter **Common Core Standards** • **CC.3.5.9-10C:** Follow precisely a complex, multistep procedure when carrying out experiments, taking measurements, or performing technical tasks. **Art** • **9.1.8.I** Know where arts events, performances and exhibitions occur and how to gain admission • **9.1.8.J.1** Incorporate specific uses of traditional and contemporary technologies within the design for producing, performing and exhibiting works in the arts or the works of others. *Explain and demonstrate traditional technologies (e.g., paint, tools, sponges, weaving designs, instruments, natural pigments/glazes)*

Next Generation Science Standards	**HS-PS1** Matter and Its Interactions • **HS-PS1-1** Use the periodic table as a model to predict the relative properties of elements based on the patterns of electrons in the outermost energy level of atoms. *[Clarification Statement: Examples of properties that could be predicted from patterns could include reactivity of metals, types of bonds formed, numbers of bonds formed, and reactions with oxygen.]* [*Assessment Boundary: Assessment is limited to main group elements. Assessment does not include quantitative understanding of ionization energy beyond relative trends.*] • **HS-PS1-2** Construct and revise an explanation for the outcome of a simple chemical reaction based on the outermost electron states of atoms, trends in periodic table, and knowledge of the pattern of chemical properties. *[Clarification Statement: Examples of chemical reactions could include the reaction of sodium and chlorine, of carbon and oxygen, or of carbon and hydrogen.]* [*Assessment Boundary: Assessment is limited to chemical reactions involving main group elements and combustion reactions.*] • **HS-PS1-7** Use mathematical representations to support the claim that atoms, and therefore mass, are conserved during a chemical reaction. *[Clarification Statement: Emphasis is on using mathematical ideas to communicate the proportional relationships between masses of atoms in the reactants and the products, and the translation of these relationships to the macroscopic scale using the mole as the conversion from the atomic to the macroscopic scale. Emphasis is on assessing students' use of mathematical thinking and not on memorization and rote application of problem-solving techniques.]* [*Assessment Boundary: Assessment does not include complex chemical reactions.*]
Kit adapted from:	Douma, Michael, curator. Pigments through the Ages. http://www.webexhibits.org/pigments (accessed June 6, 2012). Institute for Dynamic Educational Development.
Kit creation date	June 6, 2012

DNAZone Outreach
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"Chemistry of Color: Pigments In Art" Overview

Educational Objectives

After completing this experiment, students should have:

- An improved ability to balance chemical reactions
- A better understanding of the nomenclature of chemical compounds
- An understanding of the relationship between the observed color of materials and the visible light absorption of materials
- An appreciation of the connections between science and art
- Increased awareness of chemical safety and disposal

Teacher Preparation Time

Apart from the DVD spectroscopy experiment, the other activities are 2-day experiments due to various filtration, suspension and drying step. A section each day should take 20-30 minutes. The instructor should plan for the class accordingly.

Class Time

Activities in this kit are two-three day long experiments due to the drying/filtering process; plan the class accordingly. You can filter the others the day of experiment. If the pigments will be used in paintings, wait one week before adding the pigments to oil to use as paint.

Assignment and questions can be used as homework or be discussed in class depending on time.

Materials Needed

- Pigments Kit (included)
- Distilled water
- Balance

Required Student Knowledge

- Reaction chemistry and balancing equations
- Color theory

Background on Pigments

Pigments are colored particles that become suspensions when mixed with water or oils to create paints. Pigments arise from the absorption of energy of the complimentary color to what the eye observes. For fluorescent and phosphorescent materials, light is emitted, but pigments are colored due to reflection of light not absorbed.

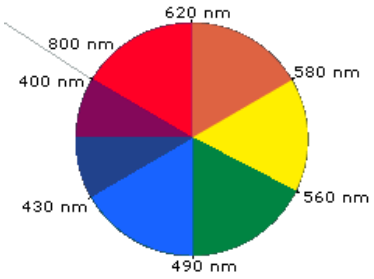


Figure 1.Color wheel Figure 2. Dragon by Anish Kapoor Figure 3. Chauvet Cave Paintings

For instance, if light containing all the wavelengths of visible light is shone on a red surface, then the surface will absorb light predominantly in the green light wavelength 490-560 nm (Figure 1), and reflect red light. Transparent colored paper works in a similar way. If light containing only red, green, and blue light passes through a filter that appears purple, the transparent filter absorbed green light. The resulting mix of red and blue light add to appear as purple.

This kind of color mixing is called subtractive mixing because colors are absorbed to have only certain colors appear. This is how paints, pigments, and transparent paper work. Additive mixing of colors occurs with colored lights and results in the appearance of new hues from the combination of light sources. This is how TVs and computer screens work, using the primary colors of light (Red, Blue, Green) to produce varied hues. The mixing is just how the eye perceives them; all colors have a true wavelength associated with them.

A spectroscope can be used to analyze the composition of light sources. A DVD spectroscope as the one provided in this kit is an easy way of viewing light. Combined with transparent sheets, the colors that pass through can be observed. For example with cyan transparent sheets, blue and green light pass through; this is observed when the red band of the spectral lines are dimmed when the sheet is placed on the slit of the spectroscope. Figure 2 shows examples of photos that can be captured of the spectral lines if students have camera phones. (The original source for the spectroscope is "A DVD Spectroscope: A Simple, High-Resolution Classroom Spectroscope" and can be found at: http://pubs.acs.org/doi/pdf/10.1021/ed083p56).

Prussian Blue along with Chinese Blue, Milori Blue and Berlin Blue are common names for complexes known as "iron blues." A Berlin color maker named Diesbach introduced the pigment in the early 1700s. By 1829 the color had spread all over Europe and to America and Japan and was being used in prints, paintings, dyes, glass, and interior paints. The color can have reddish or green undertones depending on the preparation conditions. Chinese blue has a green undertone while Milori blue is more plum colored. However, all complexes can be classified as "ferriferrocyanide pigments," or compounds containing Fe^{3+}, Fe^{2+} and CN^-. The compound is called mixed valent because it contains iron in two different oxidation states. The deep blue color

of Prussian Blue is due to a charge transfer transition between the two types of iron ions. A charge transfer transition is when electronic charge in one part of a molecule is donated or moves to another part. Also Prussian Blue has very high tinting strength. This means that when mixed with other colors/pigments, Prussian Blue strongly effects the color produced, adding lots of dark blue to the mixture. So strong tinting means that a little amount of pigment can change the color of a large amount of another paint/pigment. For instance one ounce of the pigment can tint 20 lb of lead white, and it is often mixed with yellows such as naples, ochre, and chrome to produce green paint.

From its discovery in 1706 till the 1970s, Prussian Blue has been one of the most commonly used blue pigment. Dutch easel painters began using it in early 1700s. Paintings such as the *Entombment of Christ* by Pieter van der Werff or *La Mousmé* by Vincent Van Gogh are examples of the dark Prussian Blue used in paintings. Although presently phthalocyanin blue is more common, contemporary artist Anish Kapoor has used the raw form of the pigments in mixed media sculptures and installations such as *Dragon* (Figure 2).

Red Ochre is one of the oldest known pigments used by man. Early uses in cave paintings such as the Chauvet Caves in France (Figure 3) and many others show it was easily adapted from raw materials found in nature. Clay mixed with water or fats produced dark red pigment paints that have lasted through time. Many indigenous cultures of Africa and the Americas still use Red Ochre from the earth as means of creating masks and body paint.

Decomposing iron salt compounds can also create synthetic red ochre pigments that chemically are iron (III) oxide Fe_2O_3. Most industrial methods still take clay earth samples to mine for iron ores, but for smaller scale situations and other experiments, synthetic iron oxide can be created. In this experiment iron ions of Fe^{2+} and Fe^{3+} will be reacted with NaOH to form iron hydroxides that form varying hues of brown and reds.

Malachite is also a very old pigment derived from mineral ores. It is related to azurite ores, which are copper carbonate ores that are dark blue colors. Malachite is green and the natural ore resembles the rings on a cut tree stump. The extracted pigment was used in paintings in ancient Egypt and as eye make-up for royalty. It was used up until the 18^{th} century when other synthetic green pigments began to be developed and it became less prevalent. One example is *Nativity* by Pietro Perugino, where malachite pigment was used in the green shirt of the painting (Figure 4). Many examples of malachite can be found in jewelry and stone gem objects made from the natural mineral stone.

Figure 4: Malachite used for the green shirt

Malachite is $Cu_2(OH)_2CO_3$ and is often found near sources of limestone as well, limestone being the source of CO_3^{2-} in the malachite. A similar change will be implemented for the students as they will react copper (II) sulfate with sodium bicarbonate. Notice the charge of the copper does not change and color change arises from molecules bound to the copper rather than a new ionic state.

References:

Douma, Michael, curator. Pigments through the Ages. http://www.webexhibits.org/pigments (accessed June 6, 2012). Institute for Dynamic Educational Development.

Rose, John. Pigments: Historical, Chemical, and Artistic Importance of Coloring Agents. http://www.jcsparks.com/painted/pigmentchem.html (accessed June 6, 2012).

Wikipedia ("Ochre:). http://en.wikipedia.org/wiki/Ochre (accessed June 6, 2012).

Questions or concerns?

Please visit our website at http://www.cmu.edu/cnast/outreach-dnazone/ to learn more about DNAZone or to find contact information.

An Introduction to Chemical Safety and Waste Disposal

Chemical exposure: before the start of every experiment, the student should know what he/she will be handling. Certain chemicals are flammable (e.g. ether, methanol), strongly basic or acidic (e.g. concentrated sodium hydroxide or sulfuric acid), oxidizing (e.g. hydrogen peroxide), or particularly hazardous (e.g. potassium cyanide, various heavy metal such as chromium, chloroform; more on PHS below). One good way to learn about properties of a chemical is through its material safety data sheet.

Chemical handling: use appropriate personal protective equipment (PPE). Standard PPE include lab coat, goggles, and nitrile gloves; long pants and closed toe shoes are also required. Occasionally special attentions are required, e.g. double-gloving, face mask.

Chemical spills: when chemicals are spilled, the student should first ensure no further chemicals would be spilled, notify the laboratory instructor/teaching assistant, and clean up immediately. Use a spill kit if necessary.

Reagents: do not return unused reagents or solvents back into the original container for two reasons: (1) Once the reagent/solvent is out of the container, it can be contaminated in any means; the atmosphere, for instance, can oxidize the reagent. Therefore by returning unused reagents to the original container one can contaminate the rest of the unexposed reagents. (2) There is also the probability of the mixing of the reagent with an incompatible contaminant. For instance, it is dangerous to return hydrogen peroxide to its original container with trace amounts of ether. Explosion is the likely outcome in that scenario. (https://www.youtube.com/watch?v=XafCSYMG2jg&ab_channel=hazmatty3614)

Chemical storage: the general rule of thumb is to store chemicals in dark and cool space. If necessary (usually instructed on the label of the container), they may have to be wrapped in aluminum foil, or be stored in a refrigerator/freezer.

Solid waste: dispose solid waste into the solid waste container, not the trash can! Solid waste includes filter paper, solid reagents, etc.

Liquid waste: liquid waste is usually separated into aqueous waste and organic waste due to their different properties, solubility and disposal method. In this experiment, only aqueous waste is produced, as inorganic compounds are dissolved in water. The pH of the aqueous waste should be adjusted to be between 2 and 12 by diluting with water.

Particularly Hazardous Substance (PHS): A PHS is a chemical compound that is carcinogenic, highly toxic, or a reproductive toxin. A carcinogen is cancer-causing; such an example would be chloromethane (CH_3Cl), methylene chloride (CH_2Cl_2) or chloroform ($CHCl_3$). The chemicals can modify one's genetic materials through various means, such as alkylation of thymine. An example of a highly toxic compound is potassium cyanide (KCN), which is a byproduct in this experiment and must be treated carefully. When KCN is acidified (such as inside one's stomach), HCN gas is produced. Cyanide is an inhibitor of cellular respiration and blocks the activity of mitochondria cytochrome c oxidase. Death follows by hypoxia of neural tissue. Therefore, this solution must be kept in very basic conditions to prevent the protonation of cyanide ions.

Reproductive toxins can cause miscarriages or birth defects. Some examples would be lead, dibromochloropropane (DBCP) and ethylene oxide. PHS should be disposed in the appropriate PHS waste container.

Material Safety Data Sheet (MSDS): MSDS provide useful information about the properties and potential hazardous of chemical compounds being handled. It is important to understand the potential hazardous of the starting materials and reagents, products, and byproducts. Sample MSDSs of NaOH (a reagent used in this experiment) and KCN (a byproduct) are attached.

SIGMA-ALDRICH sigma-aldrich.com

SAFETY DATA SHEET

Version 3.16
Revision Date 04/29/2015
Print Date 05/12/2015

1. PRODUCT AND COMPANY IDENTIFICATION

1.1 Product identifiers

Product name : Sodium hydroxide

Product Number : S8045
Brand : Sigma-Aldrich
Index-No. : 011-002-00-6

CAS-No. : 1310-73-2

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich
3050 Spruce Street
SAINT LOUIS MO 63103
USA

Telephone : +1 800-325-5832
Fax : +1 800-325-5052

1.4 Emergency telephone number

Emergency Phone # : (314) 776-6555

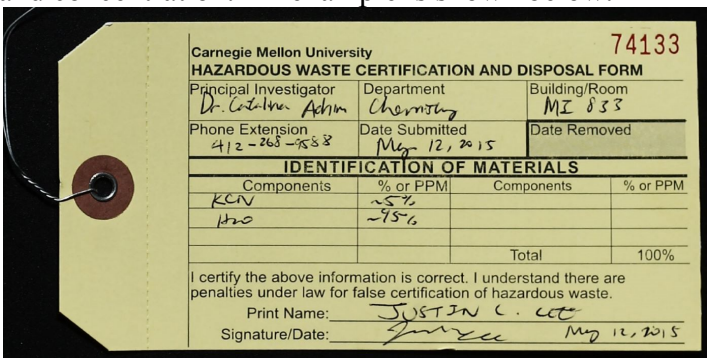
2. HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)
Corrosive to metals (Category 1), H290
Skin corrosion (Category 1A), H314
Serious eye damage (Category 1), H318
Acute aquatic toxicity (Category 3), H402

For the full text of the H-Statements mentioned in this Section, see Section 16.

Waste container label: each waste container should be labeled properly with the appropriate disposed chemical and concentration. An example is shown below.



Carnegie Mellon University 74133
HAZARDOUS WASTE CERTIFICATION AND DISPOSAL FORM

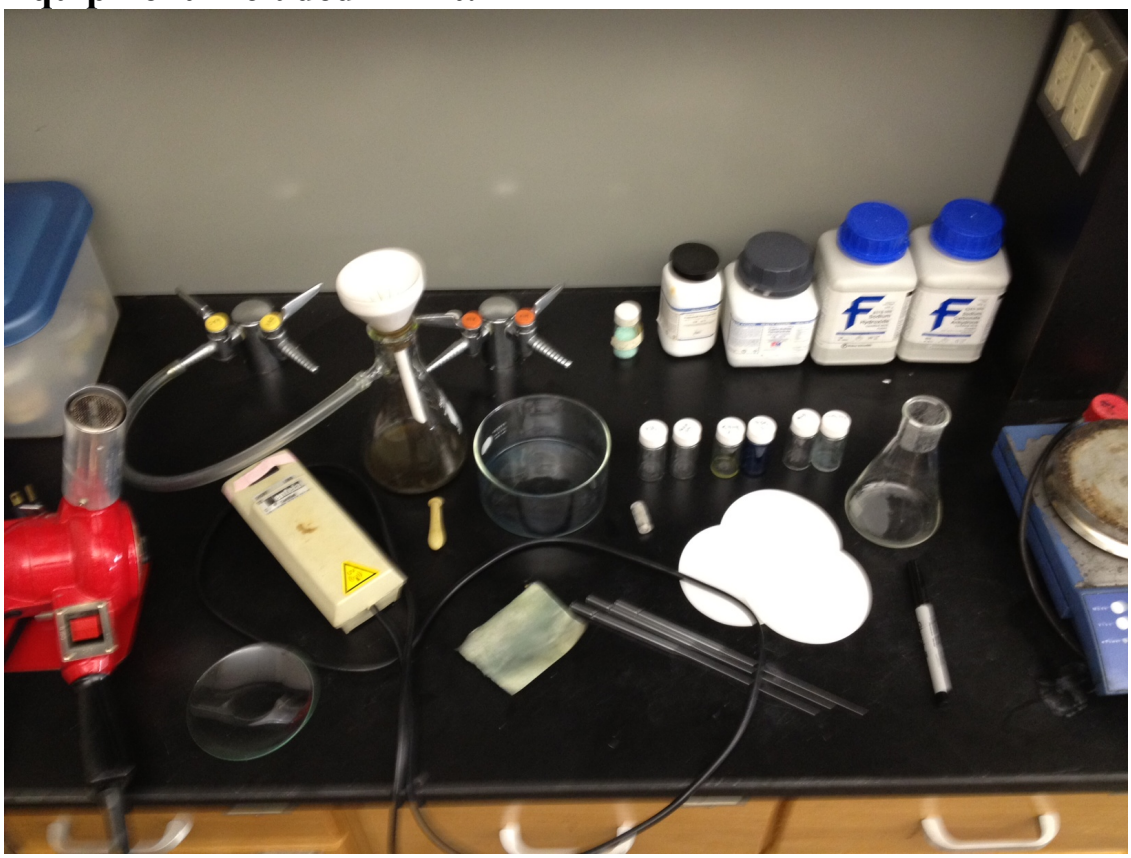
Principal Investigator	Department	Building/Room
Dr. Catalina Achim	Chemistry	MI 833
Phone Extension	Date Submitted	Date Removed
412-268-7588	May 12, 2015	

IDENTIFICATION OF MATERIALS

Components	% or PPM	Components	% or PPM
KCN	~5%		
H2O	~95%		
		Total	100%

I certify the above information is correct. I understand there are penalties under law for false certification of hazardous waste.
Print Name: JUSTIN C. CCC
Signature/Date: May 12, 2015

Equipment Included in Kit:



(Materials used for lab tets, adapted materials for class listed below)

An overview of the materials:

- 60 5 mL vials
- 24 20 mL vials
- 36 50 mL vials
- 30 Tongue depressors for stirrers
- 24 Stirrers that fit in 20 mL vials
- Al foil
- 2 boxes with safety gloves, Small and Medium
- 30 Droppers to use as pipettes
- 12 Plastic funnel
- 1 box Filter paper
- 1 Edvotek 969 Long Wave UV Light
- 8 small balances with batteries
- 8 black markers

Chemical Compounds:

- 2.5 g Iron(III) Chloride ($FeCl_3$)
- Sodium Hydoxide (NaOH)
- 12 g Iron(II) Sulfate ($FeSO_4 \cdot 7H_2O$)
- 6g Potassium Ferricyanide ($K_3[Fe(CN)_6]$)
- 7.2 g Copper(II) Sulfate ($CuSO_4 \cdot 5\ H_2O$)
- 6 g Ferric(III) Ammonium Citrate
- 3 g Sodium Carbonate (Na_2CO_3)

Malachite

$2\ CuSO_4 + 2\ Na_2CO_3 + H_2O \rightarrow Cu_2(OH)_2CO_3 + 2\ Na_2SO_4 + CO_2$

Materials:

- 5-mL vial containing $CuSO_4 \cdot 5H_2O$
- 5-mL vial containing Na_2CO_3
- 2-20 ml vials
- 1 dropper
- Filter paper
- Plastic funnel
- Aluminum foil

Procedure:

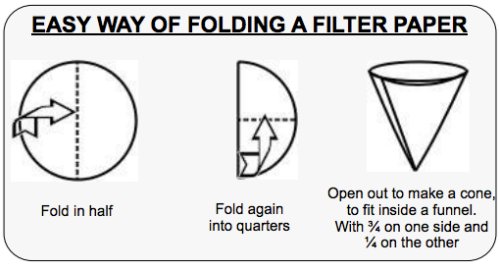
1. Wear safety gloves.
2. Prepare a solution of copper sulfate in water. Add 2 ml H_2O to the 0.6g $CuSO_4$ 5 H_2O in the 5 ml vial.
3. Add 2.2 ml H_2O to the 0.25g Na_2CO_3 in the 5 ml vial.
4. Slowly add the sodium carbonate solution to the copper solution using the dropper.

Stir vigorously as cloudy precipitate forms and then begins to bubble. Be careful if the solid mixture begins to rise over top.

5. Cover with aluminum foil and let sit over night in a cold (but not freezing) area.

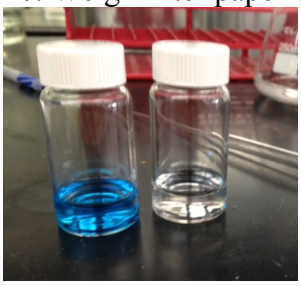
Next day:

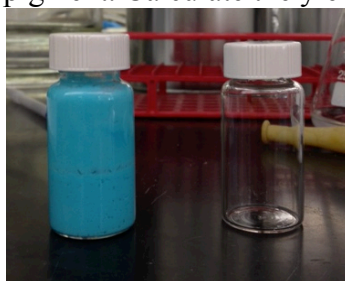
6. Weigh a round filter paper.
7. Fold the round filter paper in half. Fold it in half again so it is a quarter of a circle. Now open up the folded paper to form a conical shape and fit into plastic funnel (see figure).
8. Pour solution with precipitate into funnel over a waste 100 ml beaker.

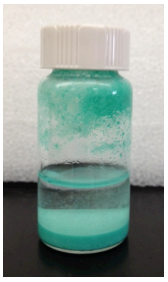


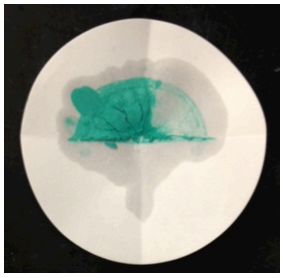
Adopted from: http://www.harrisfilters.com/downloads/24cmPapers.pdf

9. Let the precipitate sit overnight to dry in air.
10. Weigh filter paper with pigment. Calculate the yield.


Solutions of Copper Sulfate and Sodium Carbonate on left and right, respectively.


Solution immediately after mixing


Crystals formed after the vial was left overnight in refrigerator.


Malachite after filtration

Prussian Blue

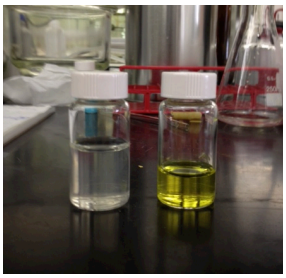
$$3FeSO_4 + 4K_3Fe(CN)_6 \rightarrow Fe^{III}[Fe^{III}Fe^{II}(CN)_6]_3 + 3K_2SO_4 + 6KCN$$

Materials:

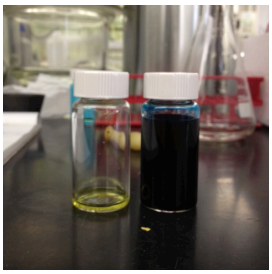
- $FeSO_4 \cdot 7H_2O$
- $K_3Fe(CN)_6$
- 2 50 ml beakers
- 1 100 ml beaker
- 2 droppers
- Filter paper
- Plastic funnel

Procedure:

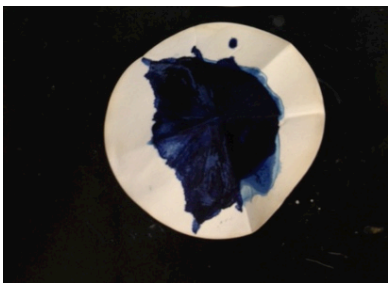
1. Add 5 ml water to 0.1g $FeSO_4 \cdot 7H_2O$.
2. Add 2.5 ml water to 0.16g $K_3Fe(CN)_6$
3. Add the $K_3Fe(CN)_6$ solution to the $FeSO_4$ solution drop by drop and mix. Try adding a drop only at first and observe precipitate; then add more.
4. Let solution sit for 30 minutes for crystals to form.
5. Fold the filter paper as described above and pour the solution through the paper in the funnel over a 100 ml waste water beaker
6. Let filtrate dry for overnight and then weigh and calculate the yield.



$FeSO_4$ on left
$K_3Fe(CN)_6$ on right



Solutions immediately after mixing



Filtered Prussian Blue

***** IMPORTANT NOTE: in this experiment, KCN is produced; it is a highly toxic compound and has an LD_{50} of 5mg/kg. Do not place the KCN waste in an acidic environment, but dilute the waste with plenty of water. The diluted KCN waste should be disposed into a separate waste container, which is provided.**

Cyanoprint with Prussian Blue

$K_3Fe(CN)_6$ + $Fe(NH_4)$(citrate) → $Fe[Fe(CN)_6]$

3 Fe^{2+} + 2 $[Fe(CN)_6]^{3-}$ → $Fe_3[Fe(CN)_6]_2$

Materials:

- $K_3Fe(CN)_6$
- $Fe(NH_4)(C_6H_5O_7)$
- 1 50 ml beaker
- A tray or small dish
- Drawing paper
- Brush
- Heat Gun
- UV Light

Procedure:

1. Each team member should obtain a piece of watercolor paper.
2. Prepare the following solution,
   0.6 g ferric ammonium citrate
   0.3 g potassium ferricyanide
   10 mL of water
3. Place the paper in one of the plastic trays under the hood. Pour some of the solution onto the paper to completely cover it. Brush over to cover both sides.
4. Dry the paper using a heat gun.
5. When dry, cover it with an opaque object such as a coin, key, paper clip, leaf, or photographic negative, and expose it to intense sunlight or to black light (long wavelength) for five minutes. (The object must be secured tightly in place to the paper. You can leave it on the window seal for a day and track the changes in color of the paper on the parts now obscured by the object.)
6. Remove the objects taped to the paper and wash the paper with a gentle stream of tap water to remove the soluble, unreacted, light-sensitive chemicals.
7. Dry the blueprint with a heat gun or let dry overnight in a dark place and attach it to your lab notebook.

Iron Hydroxide Red/Brown

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

Materials:

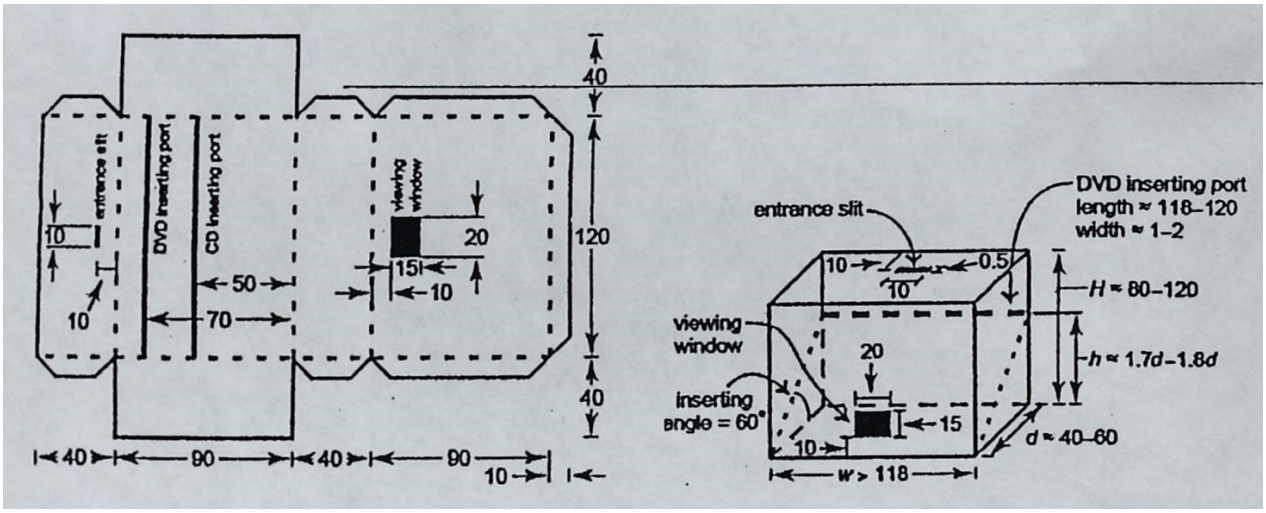
- $FeCl_3$
- $FeSO_4 \cdot 7H_2O$
- NaOH solutions of 0.5M, 1.0M and 3.0M
- 4 50 ml beakers
- 2 droppers
- 1 100 ml waste beaker
- 4 pieces of filter paper
- Plastic Funnel
- Litmus paper

Procedure:

1. Make a solution of ferric chloride in water. Add 0.2g ferric chloride and 5 ml H_2O in a 50 ml beaker
2. Add drop by drop the 0.5M NaOH until dark red precipitate starts to form. Should be around 12 ml.
3. Prepare two solutions of ferrous sulfate in water. Add 0.3g of ferrous sulfate with 10 ml H_2O in another 50 ml beaker. Do this twice more with two other 50 ml beakers
4. Add drop by drop the 0.5M NaOH solution to the first beaker, 1.0M NaOH to the second, and 3.0M to the third. Should add around 12 ml of each NaOH solution to each. Have a dropper for each molar solution of NaOH; don't mix droppers.
5. Check the pH of all 4 solutions with litmus paper and note the approximate pH value.
6. Filter each precipitate with folded filter paper in the plastic funnel
7. Let each pigment dry overnight. Observe the color when first filtered and after left to dry. Be careful with the $Fe(OH)_3$ pigment; it degrades to dried black flakes if left in air for too many days.

DVD Spectroscope Procedure

1. Insert the DVD reflective side up into the open slit on the back of the black box included in the pigment kit.
2. Point the tiny slit on the top of the box towards a window with sunlight and view through the open rectangle of the side of the box. Do not view from directly at the sun; indirect sunlight will still work. Observe what is seen.
3. Now point the slit towards fluorescent lights in the classroom and observe what is seen. What is different?
4. Take the colored transparent sheets and observe what colors are observed when overlapping two at a time.
5. Now place the sheets over the slit of the spectroscope and observe what lines of the spectrum are present and absent.
6. Using a camera or cell phone with camera, take a picture of the spectrum without or with different filters placed in front of the light entry slit. Compare side by side the spectra and the intensity of different color regions. Make approximations of the wavelengths of lines based on the visible region, with 370 nm being the blue end and 720 nm being the red end.



Questions During the Lab

Please contact DNAZone outreach coordinators to get Teacher Answer Key.

1. Balance the equations for each reaction of pigments

2. Based on the balanced reaction and molecular weights, calculate the grams of each reactant needed and verify with mass specified in procedure.

3. Weigh dried pigments to calculate percent yield recoveries.

4. What is the difference between subtractive and additive color mixing?