Chromatics - The Science of Color

March 6, 1998

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This unit relates to the following NSES physical science content standards in grades 5-8:

Transfer of Energy

1. "Energy is a property of many substances and is associated with heat, light, electricity, mechanical motion, sound, nuclei, and the nature of the chemical. Energy is transferred in many ways."
2. "Light interacts with matter by transmission (including refraction), absorption, or scattering (including reflection). To see an object, light from that object- emitted by or scattered from it - must enter the eye."
3. "In most chemical and nuclear reactions, energy is transferred into or out of a system. Heat, light, mechanical motion, or electricity might all be involved in such transfers."
4. "The sun is a major source of energy for changes on the earth's surface. The sun loses energy by emitting light. A tiny fraction of that light reaches the earth, transferring energy from the sun to the earth. The sun's energy arrives as light with a range of wavelengths, consisting of visible light, infrared, and ultraviolet radiation."

This unit relates to the following NSES physical science content standards in grades 9-12:

Conservation of Energy and the Increase in Disorder

5. "The total energy of the universe is constant. Energy can be transferred by collisions in chemical and nuclear reactions, by light waves and other radiations, and in many other ways. However, it can never be destroyed. As these transfers occur, the material involved becomes steadily less ordered."

Interaction of Energy and Matter

6. "Waves, including sound and seismic waves, waves on water, and light waves, have energy and can transfer energy when they interact with matter."
7. "Electromagnetic waves include radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays. The energy of electromagnetic waves is carried in packets whose magnitude is inversely proportional to the wavelength."
8. "Each kind of atom or molecule can gain or lose energy only in particular discrete amounts and thus can absorb and emit light only at wavelengths corresponding to these amounts. These wavelengths can be used to identify the substance."

1. The Science of Color

The nature of color is intimately related to light and the interactions of light with matter. Therefore, the nature of light has to be examined first. Light is a form of energy that is propagated like a wave, similar to the waves in the ocean. Waves have a wavelength, which is the distance from crest to crest, and a frequency which is the number of waves that pass a given point per second. But there are many differences between light waves and other waves. Unlike a wave in the ocean or a sound wave, light waves do not need a medium such as water or air for propagation. Light is transmitted through a perfect vacuum.

Everyone has observed that a stick protruding from a body of water appears to have a kink in it at the surface of the water. Try it with a pencil in a glass of water. This is because the speed of light is different (slower) in water than it is in air. According to Fermat's principle, light follows the path that minimizes its time to pass from point A to point B. When the path includes media with differing indices of refraction, this requires that the light path bend at each interface. This is known as refraction. The difference in the speed of light in different materials relative to that in a vacuum is expressed as the index of refraction of the material.

Light can also be scattered by small particles in the air. That is why dirty water appears cloudy and why visibility is limited on a smoggy day. When this phenomenon operates differently on different wavelengths of visible light, colors are produced.

Color arises from a variety of causes, both physical and chemical in origin. These causes will be explored throughout this module and are summarized in Figure 1-1. In general, physical origins of color are those that can be traced to the wave nature of light interacting with matter, while the chemical origins of color relate to the interaction of light with electrons to produce transitions in energy states. Examples of physical origins of color include scattering, interference, diffraction, and refraction. Examples of chemical origins of color include selective absorption of wavelengths by chemical bonds that can produce colors seen in reflection or transmission. In some cases, the absorbed electrons move into excited (or metastable) states where they produce emitted colors by decay to a ground (or stable) state. The physical and chemical origins of color are summarized in Figures 1-2 and 1-3.

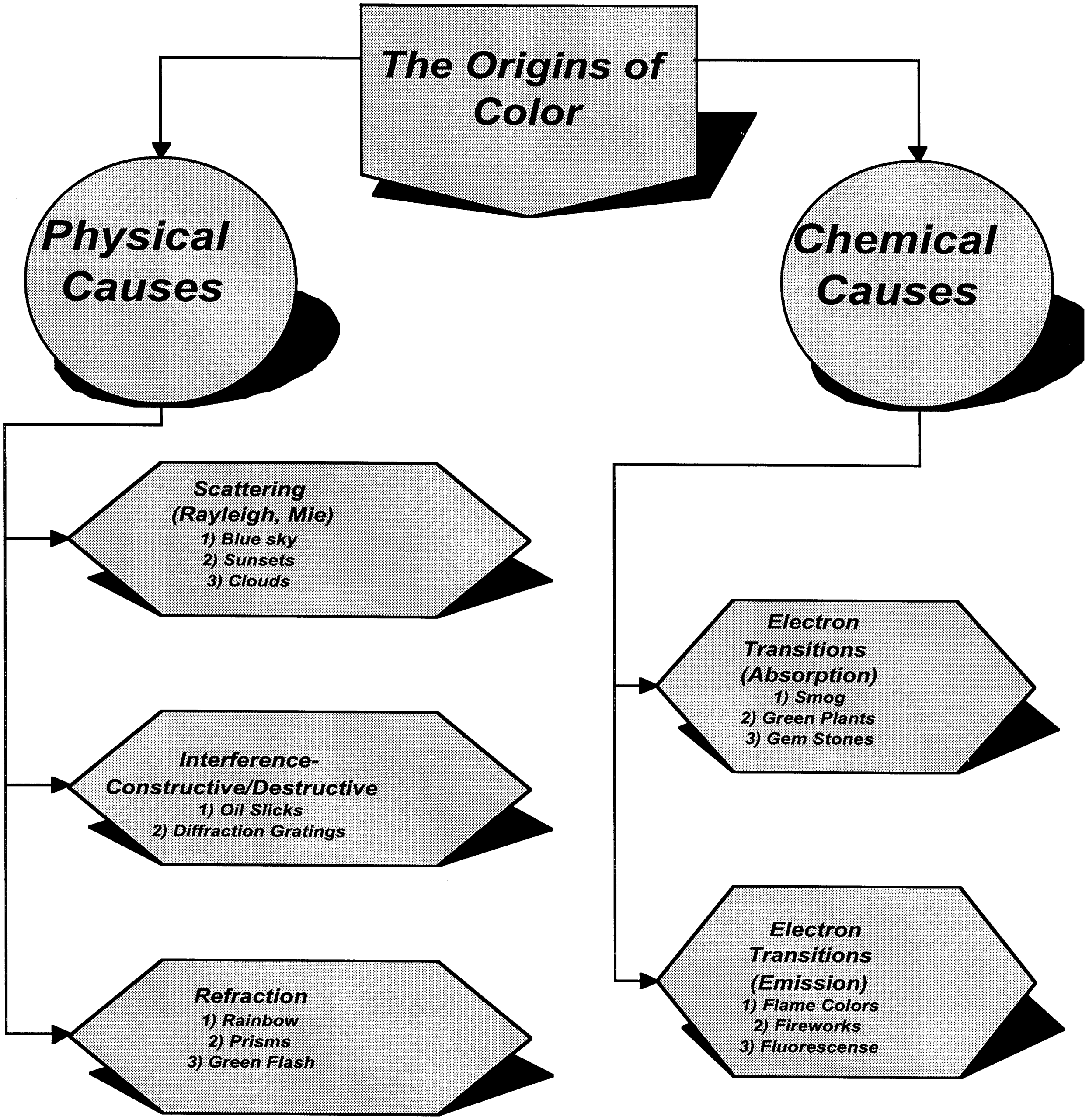
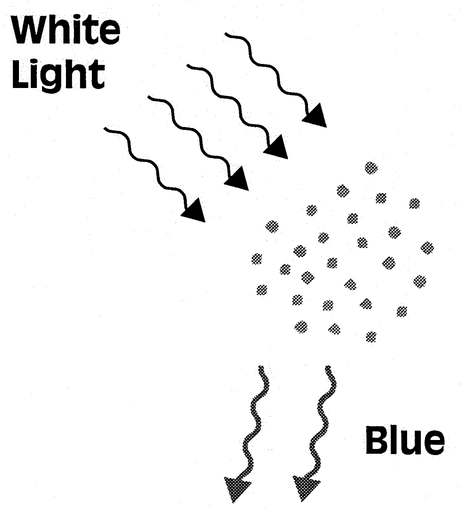
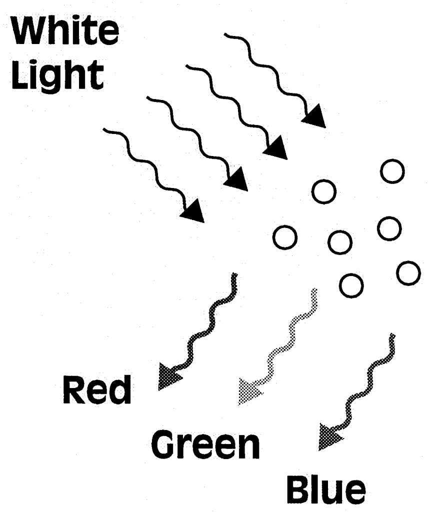


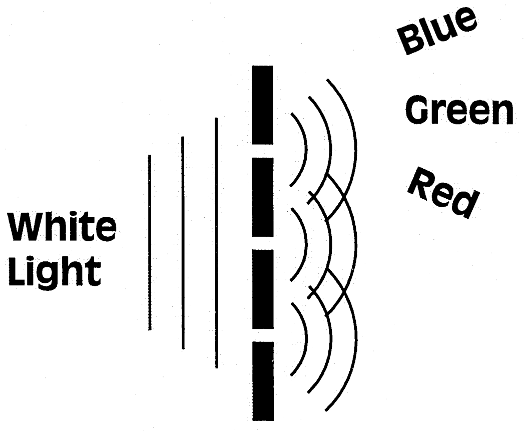
Figure 1: The Origins of Color



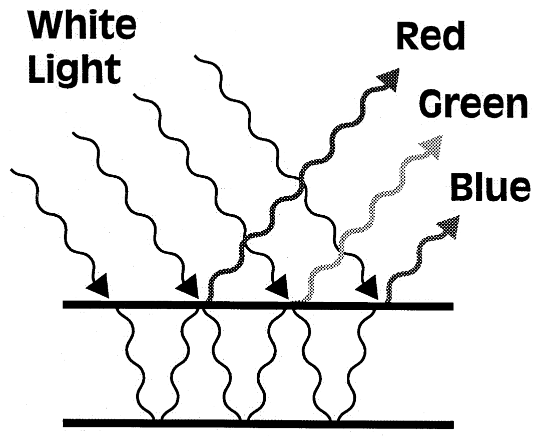
Rayleigh scattering causes the blue sky



Refraction causes the rainbow



Diffraction disperses white light into constituent colors



Interference causes colors of oil on water

Figure 2. ***Some of the physical causes of color include scattering, refraction, diffraction, and interference***

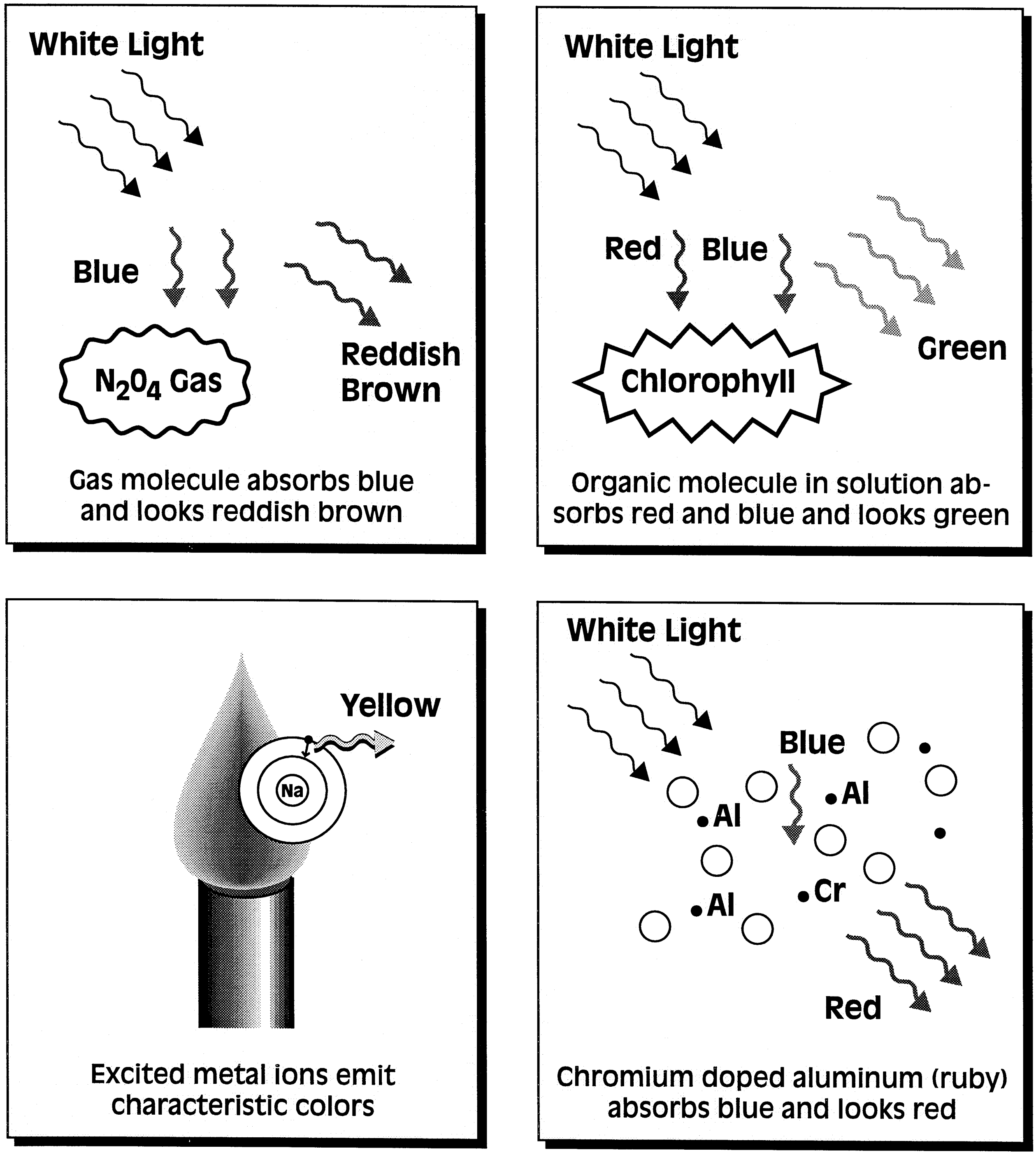
Light is just one small segment of a wide electromagnetic spectrum that includes radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays, gamma rays, and cosmic rays. The frequency correlates directly with energy and inversely with wavelength; the higher the frequency, the higher the energy of the photon; the longer the wavelength, the lower the energy. Cosmic and gamma rays, followed by X-rays are the most energetic photons and radio waves are the least as shown in Figure 1 on laboratory 1-1.

Why is the visible part of the spectrum in the region where it is? To answer that question we must first examine how light interacts with matter. All matter is made of atoms which contain electrons and these electrons are in discrete orbitals. A photon of the proper energy can interact with the electrons and be absorbed. Because electrons can only be found in discrete orbitals or energies, the energy of the absorption has to correspond to the energy difference between orbital states. If the energy of the photon is too low, such as in the infrared or microwave region, the photon cannot cause an electronic transition between orbitals and the photon may simply pass through the material as if it were not there. We are surrounded by low energy electromagnetic radiation in our daily lives that pass through matter including buildings and our bodies. For example, radio waves are all around us and can easily be detected by turning a radio on, which is equipped with an antenna to capture the energy. You can try to shield the antenna with your body, or put it in a light structure like a wooden garage, but it will continue to receive radio waves. On the other hand, if the energy of an electromagnetic wave is high enough, it will be absorbed and break bonds in organic molecules. An example of this kind of ionizing radiation is x-rays. The human eye contains structures in the retina called rods and cones where chemical reactions occur in response to light that allow us to detect light and color. The portion of the electromagnetic spectrum that is sufficiently energetic to cause reversible changes to the rods and cones in the eye, but not so energetic as to cause permanent changes is referred to as the visible spectrum or visible light and it comprises all the colors that we can see. Each color of the spectrum is associated with a specific frequency or narrow frequency range of light. However, the human eye responds to color in its own unique way and actually interprets color based on it own set of rules. This module addresses how the eye perceives color and how the primary additive colors, red, blue, and green, and the primary subtractive colors, cyan, yellow, and magenta interact to provide a wide range of colors in a simple series of demonstrations and experiments.

The manner in which electrons in atoms and molecules interact with light depends on the environment the atoms or molecules are in. Specifically, the electronic state and the available orbitals are critical and these are determined by the electronic structure of the element involved and how it is bonded to its neighboring atoms. The type and strength of bonding is different in gaseous, liquid, and solid matter. These effects are some of the chemical causes of color which are highlighted in Figure 2. This module addresses some of the fundamental aspects of color in the three states of matter in several simple experiments.

In gases the electronic states are limited, because there are relatively few atomic and molecular gaseous species and correspondingly few orbital transitions. This limits the color causing phenomena found in gases, although refraction and scattering are physical causes that can occur if large bodies of gases are involved, such as in the earth's atmosphere. A much larger range of atomic and molecular species and mechanisms for interaction is found in liquids leading to a wide range of color phenomena. These can involve the electronic transitions of the molecules in the liquid themselves, such as in the blue ocean water. Or it may be due to an ion of a dissolved salt or a molecule, such as in inks or colored drinks. Or it may be due to a dissolved liquid or solid in the form of a suspension, which is the case in milk or paints. Solids have the most complex electronic structures and therefore have the most varied color causing phenomena. Examples are found all around us in nature in plants, rocks, minerals, and gems; also in man-made products including paints, ceramics, plastics, building materials etc. Certain materials change color based on an external effect such as temperature or pressure. Some animals can control the amount of pigmentation in their skin or scales and have the ability to change color in response to external stimuli. These effects are presented separately in a section on Dynamic Colors.

Color is not an intrinsic characteristic of an object like size, shape or mass. Rather it is a result of the interaction of light with the object and the interaction of the light that enters the eye. This is easily demonstrated by observing colored objects under a strong light of one color, such as red or yellow. Most of the objects will appear to be nearly the same color with variations in intensity. For example, certain city lights are sodium filled and emit a strong yellow light. Cars of vastly different colors will appear similar under sodium vapor light. Objects can interact with light in three ways, absorbing, reflecting, or transmitting it; or some combination of these three. The exact way the object interacts with light and how the human eye interprets the resultant light that enters the eye is what determines an object's color.



Gas molecule absorbs blue and looks reddish brown

Organic molecule in solution absorbs red and blue and looks green

Excited metal ions emit characteristic colors

Chromium doped aluminum (ruby) absorbs blue and looks red

Figure 3. The chemical causes of color result from electrons transitioning between orbitals and absorbing or emitting photons.

Chromatics - The Science of Color

Laboratory No. 1-1

Surfing the Electromagnetic Spectrum

Purpose:

To demonstrate the relationship between color and wavelength of light.

Materials:

1. An incandescent light source (overhead projector.)
2. Mercury and neon (krypton) pen lamp
3. Diffraction grating or a prism and slit (two tablets of paper).

Discussion:

What we see as visible light actually comprises a very small portion of the electromagnetic spectrum from about 400 to 700 nm (400×10^{-9} - 700×10^{-9} m). The colors in the visible spectrum are each associated with a specific wavelength region as shown in Figure 1. A light wave carries an energy with it which is proportional to its frequency. Red light has the longest wavelength and shortest frequency and is the least energetic component of the visible spectrum. Blue light, at the opposite end of the spectrum, is the highest energy radiation which we can see.

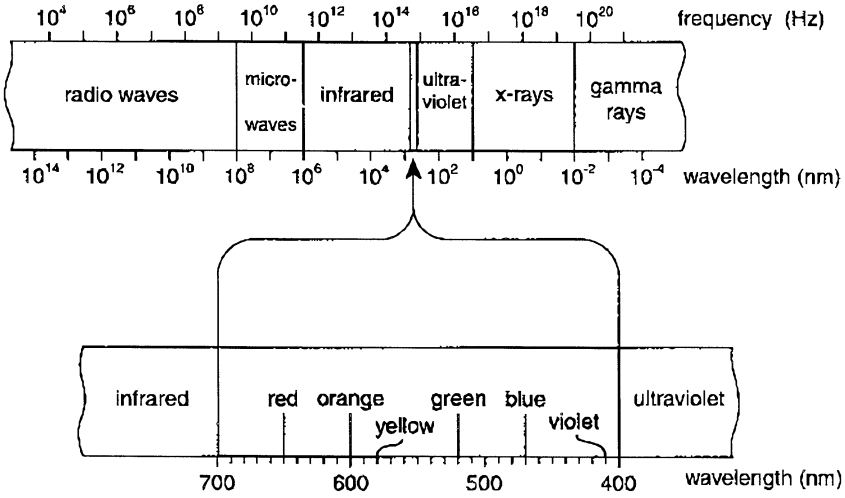


Figure 1. Visible light comprises a very small component of the electromagnetic spectrum.

Color is how we sense the energy carried by a light wave. Our eyes contain two types of special detectors that are sensitive to visible light. These were named rods and cones after their structural shape. Figure 2 shows the sensitivities of rods and cones to visible wavelengths. Rods enable us to see at night; although rods are very sensitive to light, they cannot distinguish color. Cones are responsible for color vision and are divided into three classes which absorb primarily either red, green, or blue light. They are less sensitive to light than rods, which is why we cannot see colors at night. Equal stimulation of all three cones yields white light. Non-uniform stimulation of the three cones can result in the ability of the eye to distinguish up to ten million colors.

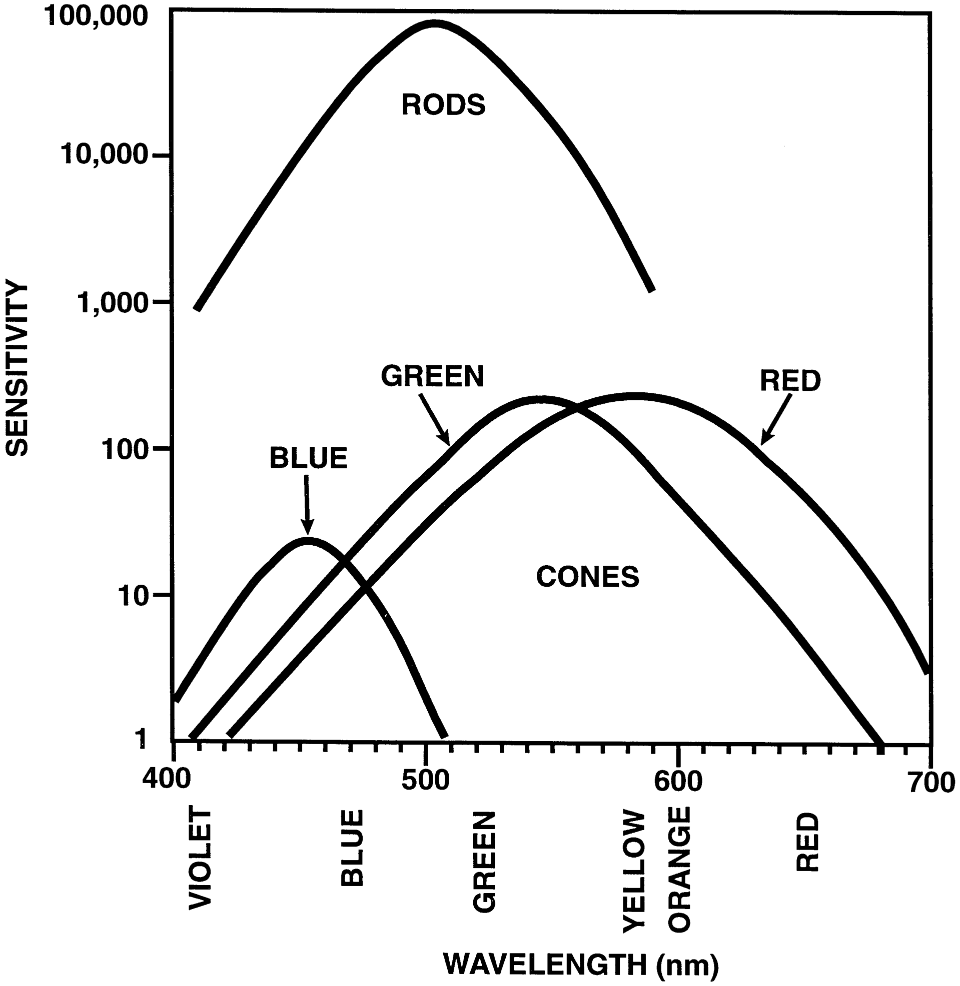


Figure 2. The sensitivity of the rods and cones of the human eye in arbitrary units as a function of wavelength of light. The rods in our eyes are very sensitive to light and enable us to see at night while the three types of cones give us color vision during the day.

Our eyes are not sensitive to waves with energies outside the limited region defined as the visible spectrum. Infrared light has too low an energy to excite a chemical reaction in our rods and cones. However, we can detect IR radiation as heat! Ultraviolet light is too energetic and actually damages our cells; we may "see" UV light indirectly through the mechanism of fluorescence, which is discussed in Section 4. Certain insects and animals have developed eyes which may see other "colors" outside our limited range, including infrared radiation, in order to survive. Night vision devices employed by law enforcement and the military make objects more visible in low light situations by “intensifying” the available light.

Individual colors of the spectrum can be mixed to create the other colors in the spectrum. Red and yellow produce orange for instance and red and violet can produce various shades of purple. The greatest number of colors can be made by mixing one color from each of the two ends of the spectrum (red and blue) and one in the middle (green). Red, blue and green are known as additive primaries for this reason.

Note that mixtures of red and blue, such as magenta, are colors that we can see, but are colors that are <u>not</u> observed in rainbows. This is because the rainbow consists of colors of light in order from the lowest wavelength (blue) to the longest wavelength (red). In contrast, magenta is a color that is a mixture of blue and red.

The sun and normal incandescent light bulbs produce nearly white light by mixing all the wavelengths (colors) together. White light can be separated into its component colors, called a spectrum by passing the light through a prism or through a diffraction grating.

Materials can emit visible light when their constituent atoms or molecules heated to a sufficiently high temperature. If the emitted light is passed through a diffraction grating or prism, a spectrum of characteristic wavelengths is produced. The sun or an incandescent light bulb will produce a band of color called a *continuous* spectrum while a gas such as hydrogen will produce discrete wavelengths of light called an *emission* (bright line) spectrum. Dyes, filters, or gases may remove specific wavelengths of light while reflecting others. White light passed through a transparent material of this type will produce an *absorption* or dark line spectrum. A dark line will appear against a colored background where a specific wavelength has been removed or absorbed by the material.

Procedure:

1. Turn on the incandescent light source and direct the light onto a diffraction grating. What colors are produced?

2. Turn on the mercury lamp and direct the light onto a diffraction grating. What colors are produced?

3. Turn on the neon lamp and direct the light onto a diffraction grating. What colors are produced?

(If using a prism instead of a diffraction grating, direct the light onto a slit and then the prism to better see the output light. Darken the room if necessary.)

Questions:

1. Why did you observe the different colors in procedures 1, 2, and 3?
2. Why can't we see colors well at night?
3. What do you think will happen if you pass a red laser beam through a prism?

Answers:

1. An object's color depends upon the wavelengths of the light illuminating it.

2. Our color receptors in our eyes (cones) are not sensitive enough to distinguish color at low light levels.

3. A red laser is composed of only one frequency of light, so the red light would refract (bend) as it passed through the prism, but it would emerge from the opposite side a red beam.

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Laboratory No. 1-2

Light Emitting Colors and Their Color Mixing

Purpose:

To investigate how additive color mixing works using a color monitor or TV.

Materials Needed:

1. Color computer monitor/computer
2. 8 X magnifying glass (such as Radio Shack 30X illuminated microscope and 8X magnifier C/N 63-851)
3. Color painting or drawing software is helpful, but not necessary

Discussion:

Our eyes are sensitive to three primary colors, red, green and blue. That is because our eyes contain three different types of color receivers called cones. We each have a red cone for seeing red light, a green cone for seeing green light and a blue cone for seeing blue light. Our brain interprets different amounts of red, green and blue light that hits our eyes at once as various colors. If only red light hits our eye, we see the object as red. If equal amounts of red light and green light hit our eyes, we see yellow. If no visible light hits our eyes, we see black and if equal amounts of red, green and blue light hits our eyes, then we see white. These and other combinations are shown in table 1 below.

Note that red, green and blue are called the primary colors of light or the primary additive colors because adding these particular 3 colors in different combinations produces essentially all of the colors that we can see.

Table 1: When equal intensities of light of the colors in the first 3 columns strikes your eye, you see the color in the 4th column

RED	GREEN	BLUE	You see
			BLACK
X			RED
	X		GREEN
		X	BLUE
X	X		YELLOW
	X	X	CYAN
X		X	MAGENTA
X	X	X	WHITE

So how does this work to get all the colors using only three colors of light? Picture that you have a number of small lights consisting of the three primary colors. When red light is added to green light, your eye registers equal amounts (or parts) of red and green light. Your brain averages them to yellow. But what about orange or purple? Adding red (one part red) to yellow (one part red and one part green) results in orange. So orange is 2 parts red and one part green. Similarly, since purple is between magenta (one part red and one part blue) and blue (one part blue), purple results when more blue than red light strikes your eye.

Procedure:

1. Using some graphics software, produce solid squares of black, white, red, green, blue, cyan, magenta, and yellow on the computer monitor
2. Using the magnifying glass, look at how black, white, red, green, blue, cyan, magenta, and yellow are produced by the color monitor. Prepare a table summarizing these results.

Question:

How are red, green and blue light mixed to produce the colors black, white, red, green, blue, cyan, magenta, and yellow?

Answer:

The table should look like Table 1. The computer monitor uses an array of red, green, and blue lights to produce the wide range of colors that we observe.

Chromatics - The Science of Color

Laboratory No. 1-3

Colors That Absorb Light

Purpose:

To investigate the subtractive or absorptive properties of transparent films of different colors.

Discussion: How we see colored objects:

Recall again that the colors that we see depend on the relative amounts of red, green or blue light that shines on our eyes, as summarized in Table 1 of the previous section. Consider the three colors cyan, yellow and magenta. Each of them consists of a combination of two of the primary colors of light.

Now let's consider objects that appear to be one of the primary colors, such as a red apple. Again, the apple does not give off light, so that its color must be due to light that is reflected off of it. For the apple to appear to our eyes to be red, only red light must be reflected off the apple, so that only red light strikes our eyes. Therefore, the red apple must absorb all light other than red. In other words, it absorbs the green and the blue parts of the white light.

Thus, a red object absorbs all light other than red so that it reflects only red light back to our eyes. Similarly, a blue object absorbs all light other than blue and reflects only blue light back to our eyes. Finally, a green object absorbs all light other than green and reflects only green light back to our eyes. Now let's consider how an object such as a banana looks yellow. The banana is certainly not a source of light. We observe that it has color only when it is illuminated by room light or sunlight. Room light or sunlight is white light in that it is a mixture of all the colors, including red, green and blue light. We know this because we have seen how water or glass or a prism can produce a rainbow from sunlight or room light. The banana has color because it is illuminated by white light and some of that light is reflected by the banana back to our eyes. Let us consider in detail the color yellow. An object appears to be yellow if light coming from the object consists of an equal mixture of red and green light without any component of blue light. For a light source such as a computer monitor, yellow light was produced using red and green light.

What part of the white light has been reflected back to our eyes for us to see that the banana is yellow? The banana must have reflected equal amounts of the red and green portion of the white light back to our eye and it must not have reflected any of the blue light back to our eye. In other words, it absorbed all of the blue light. Therefore yellow (due to the reflected yellow light which entered our eye) can be viewed as the color which absorbs all of the blue part of the white light and does not absorb any of the red or green part of the white light. In other words, yellow subtracts or removes blue light from white light. Yellow is called one of the primary subtractive colors.

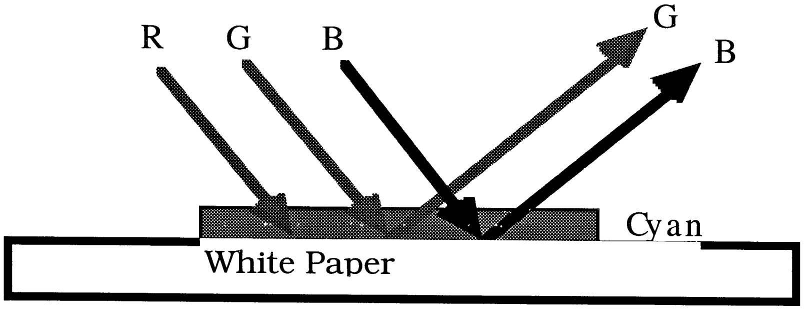
In a similar manner, from Table 1 of the previous section, it can be seen that cyan is the color which absorbs (subtracts) red light and magenta is the color which absorbs (subtracts) green light. Cyan, yellow and magenta are called the primary subtractive colors. These results are summarized in the table below.

Table 2: How we see colored objects

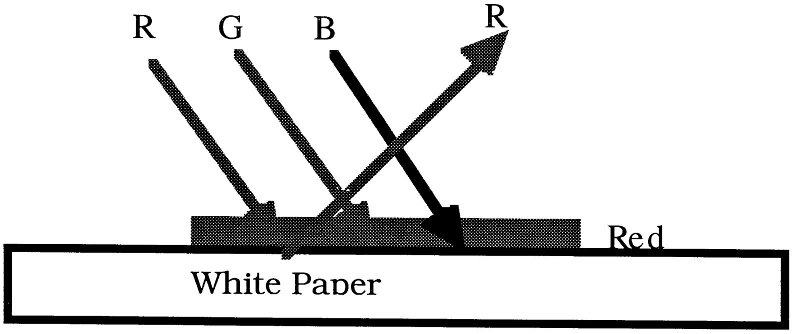
When white light strikes a surface with the color	These colors are absorbed			So these colors are reflected			So you see
	RED	GREEN	BLUE	RED	GREEN	BLUE	
WHITE				X	X	X	WHITE
CYAN	X				X	X	CYAN
YELLOW			X	X	X		YELLOW
MAGENTA		X		X		X	MAGENTA
RED		X	X	X			RED
GREEN	X		X		X		GREEN
BLUE	X	X				X	BLUE
BLACK	X	X	X				**BLACK**

Cyan absorbs red light leaving green and blue

Your eye sees green + blue as cyan



Red absorbs green and blue light
leaving red



Materials Needed:

1. Color computer monitor/computer
2. 8 X magnifier
3. Transparent films of cyan, magenta, yellow, red, green and blue
4. Using some graphics software, produce solid squares of cyan, magenta, and yellow on the computer monitor

Procedure 1:

1. Examine a white part of the computer monitor. Using the magnifier, note that it consists of red, green and blue dots. Place the cyan colored film on the monitor. Using the magnifier, notice which dot colors now look black or much darker. Since cyan absorbs red, the red dots now appear black (since all of the red light given off by the red dot was absorbed by the cyan film), while the green and blue dots appear relatively unchanged. It is helpful to look at the edge of the film using the magnifier so that you can see uncovered regions as well as regions of the monitor covered by the film. Try using both single and double thickness films.
2. Repeat step 1 using the yellow film. Which dots now appear black.?
3. Repeat step 1 using the magenta film. Which dots now appear black.?
4. Repeat step 1 using the red film. Which dots now appear black?
5. Repeat step 1 using the green film. Which dots now appear black?
6. Repeat step 1 using the blue film. Which dots now appear black?

Procedure 2:

Using some graphics software, produce solid squares of cyan, magenta, and yellow on the computer monitor. For each situation below, perform the experiment described and explain why you see the resulting color using either words or a diagram.

1. Place at least 2 layers of cyan film over the cyan square.
2. Place at least 2 layers of magenta film over the cyan square.
3. Place at least 2 layers of yellow film over the cyan square.
4. Place at least 2 layers of cyan film over the magenta square.
5. Place at least 2 layers of magenta film over the magenta square.
6. Place at least 2 layers of yellow film over the magenta square.
7. Place at least 2 layers of cyan film over the yellow square.
8. Place at least 2 layers of magenta film over the yellow square.
9. Place at least 2 layers of yellow film over the yellow square.

Results:

1.

1. The red dots appear black because cyan absorbs red light.
2. The blue dots appear black because yellow absorbs blue.
3. The green dots appear black because magenta absorbs green.
4. The green and blue dots appear black because red absorbs green and blue.
5. The red and blue dots appear black because green absorbs red and blue.
6. The red and green dots appear black because blue absorbs red and green.

2.

1. The cyan square stays cyan because cyan is a mixture of green and blue and cyan only absorbs red.
2. The cyan square becomes blue because cyan is a mixture of green and blue and magenta only absorbs green.
3. The cyan square becomes green because cyan is a mixture of green and blue and yellow only absorbs blue.
4. The magenta square becomes blue because magenta is a mixture of red and blue and cyan only absorbs red.
5. The magenta square stays magenta because magenta is a mixture of red and blue and magenta only absorbs green.
6. The magenta square becomes red because magenta is a mixture of red and blue and yellow only absorbs blue.
7. The yellow square becomes green because yellow is a mixture of red and green and cyan only absorbs red.
8. The yellow square becomes red because yellow is a mixture of red and green and magenta only absorbs green.
9. The yellow square stays yellow because yellow is a mixture of red and green and yellow only absorbs blue.

Questions:

1. White light strikes a liquid covering a reflective white sand surface. The liquid absorbs all of the red and green components of the light. What color does the liquid appear to be?

2. White light strikes a solid object. The material absorbs all of the red and blue component of the light. What color does the material appear to be?

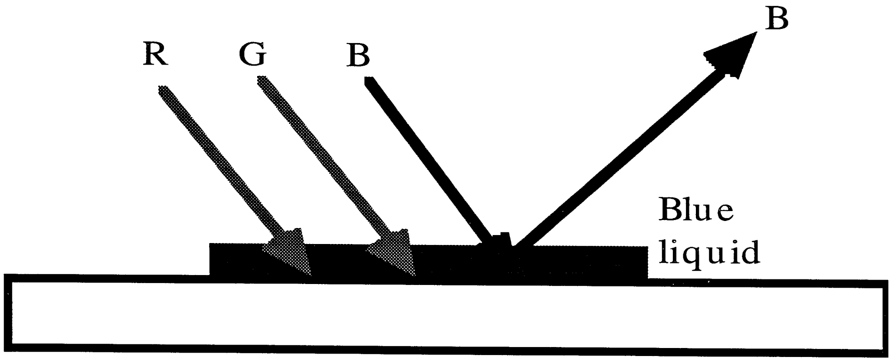
3. White light strikes a gas, which absorbs all of the blue and green components of the light. After the white light passes through the gas, what color does it appear to be?

4. A small solid body sends out (emits) white light. The white light strikes a wide but thin body of gas that scatters blue light. What color does the solid appear to be? What color does the gas appear to be?

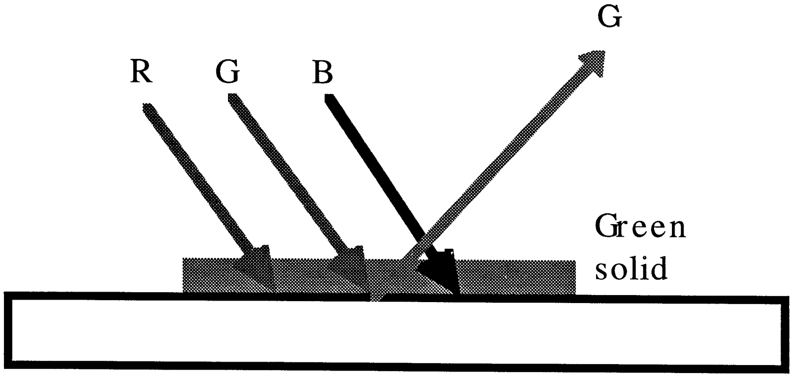
5. A small solid body sends out (emits) white light. The white light strikes a narrow but thick body of gas that scatters all of the blue light and some of the green light. What color does the solid appear to be? What color does the gas appear to be?

Answers:

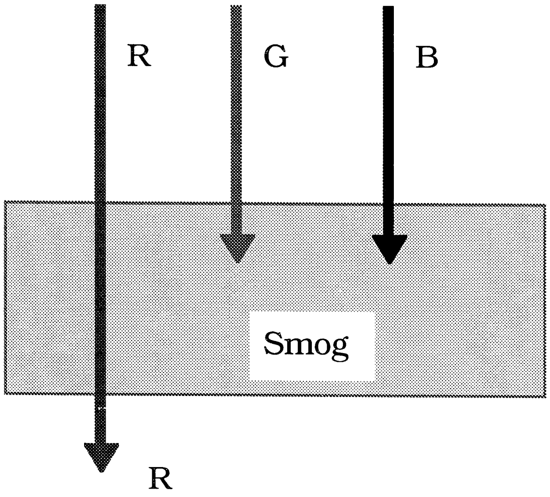
1. The liquid will appear to be blue, since the red and green components were absorbed. This is the basic color theory that explains the blue color of water.



2. The solid will appear to be green, since the red and blue components were absorbed. This is the basic color theory that explains the green color of plants.



3. The gas appears to be red, since the blue and green components were absorbed. This is the basic color theory that explains the reddish brown color of smog.



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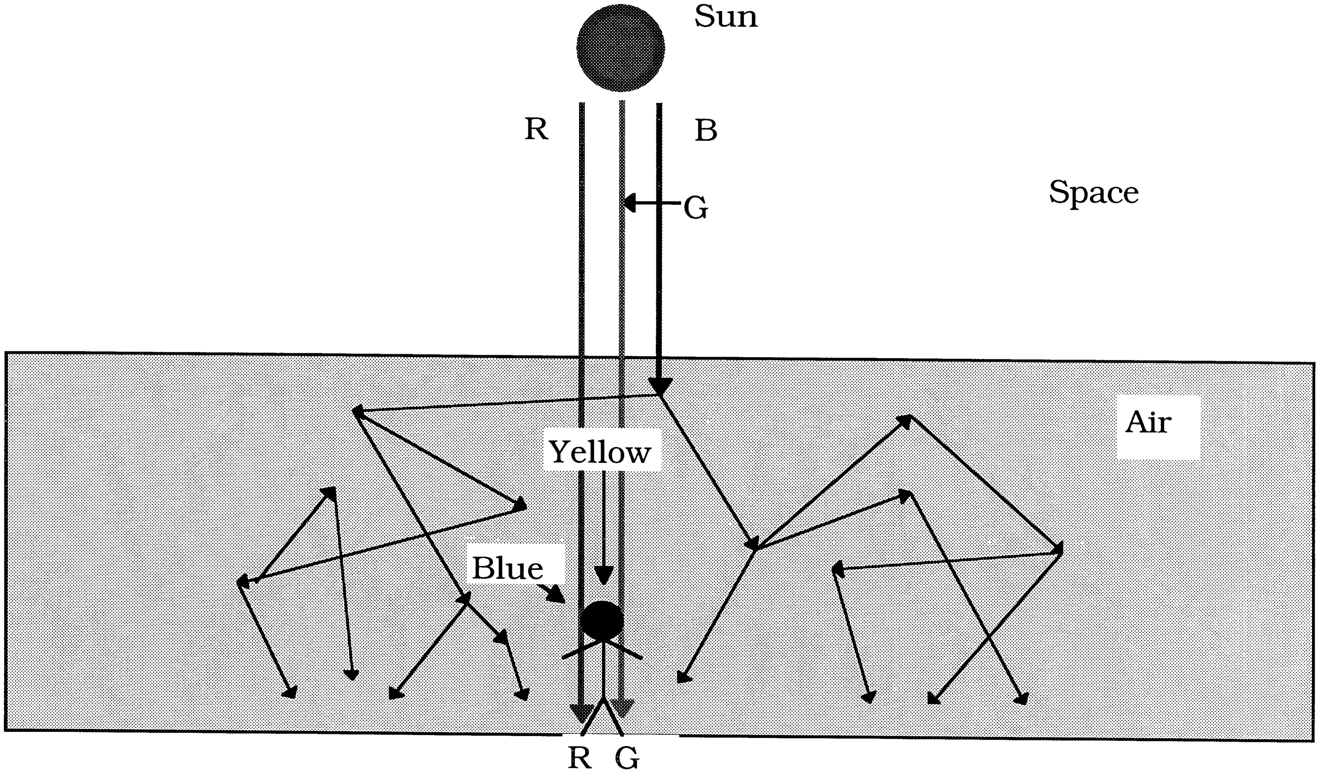
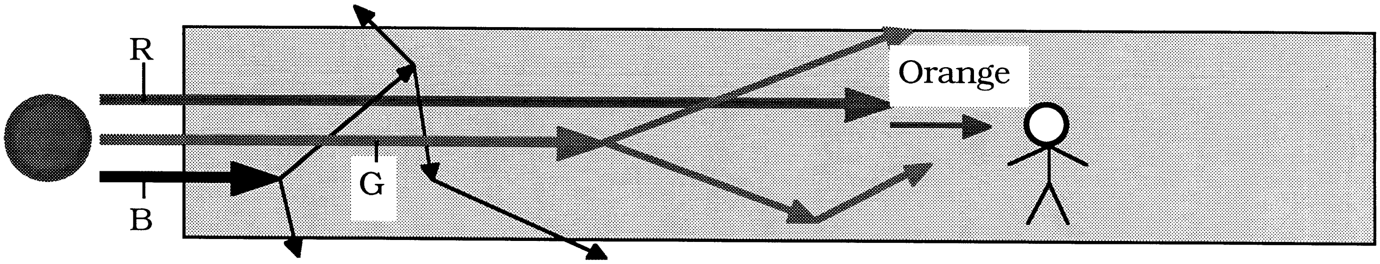
4. The small solid appears to be yellow (red+green), since the blue component was scattered. The is the basic color theory that explains the color of the sun. If you look straight up into the sun, it appears to be yellow. If you look away from the small solid object (the sun), the gas (air) appears to be blue. This is the basic color theory that explains the blue color of the sky and the yellow color of the sun.



5. The type of diagram used in Answer 4 above can also be used to explain the color theory behind the orange/red sunsets. When the sun is overhead, the sun light passes through a small amount of air, which tends to scatter the blue light. When the sun is near the horizon, the sun light must pass through a thicker layer of air, which tends to scatter the blue light strongly, the green light less strongly, and the red light hardly at all. (As we will see later, the air scatters the light with the shortest wavelength the strongest.) Since most of the red, just some of the green and almost none of the blue light reaches your eye, the entire sky as well as the sun appears red or orange when the sun sets.



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Chromatics - The Science of Color

Laboratory No. 1-4

Color Printing

Purpose:

To investigate how commercial colored pages are printed using cyan, magenta and yellow inks.

Materials Needed:

1. 30 X illuminated hand held microscope.
2. Printed colored pages from magazines, comics, cereal boxes, newspapers, etc.

Discussion:

Color printing of intermediate colors is done using a combination of adjacent and overlapping dots of cyan, yellow and magenta. The colors RGB are produced by overlapping two of the CMY inks, namely red = Y/M, green = C/Y and blue = C/M. The color black can be produced by overlapping C, Y and M. Colors between each of these can be produced by using adjacent dots of different colors. This will be explored in the next experiment.

Procedure:

1. Observe which dots produce different colors in the printed colored pages
2. Tabulate your data in the following way:

By eye	In microscope	In microscope	In microscope	In microscope	In microscope	In microscope
Color observed	Amount of cyan dots	Amount of yellow dots	Amount of magenta dots	Amount of C/Y = Green dots	Amount of C/M = Blue dots	Amount of Y/M = Red dots

3. What conclusions can you make concerning how printed colors are made?

Answers:

Printed colors are made using cyan, magenta and yellow dots. Black or grays can be made using either black ink or using cyan/magenta/yellow. Intermediate colors are produced by varying the ratio of these inks. Lighter colors are made by varying the density of the dots on the white background. Darker colors are made by increasing the density of the dots or by adding more black to the background.

Many color pages contain small samples of the primary subtractive colors cyan, magenta, and yellow so that the printer can calibrate his primary colors against standards to ensure that the correct colors are being printed. Examples may be found on the top side flap of Kellogg's Crispix cereal, the top side flap of Post Honey Bunches of Oats cereal, the top side flap of Girl Scout Thin Mint cookies, and on bottom of many pages of Parade Magazine, a supplement to most Sunday newspapers, and many other places. Ask your students to find examples and bring them to class to share and discuss.

Chromatics - The Science of Color

Laboratory No. 1-5

Fermat's Principle of Least Time

Purpose:

To understand reflection, refraction and dispersion (how a prism works) using a simple yet powerful unifying principle.

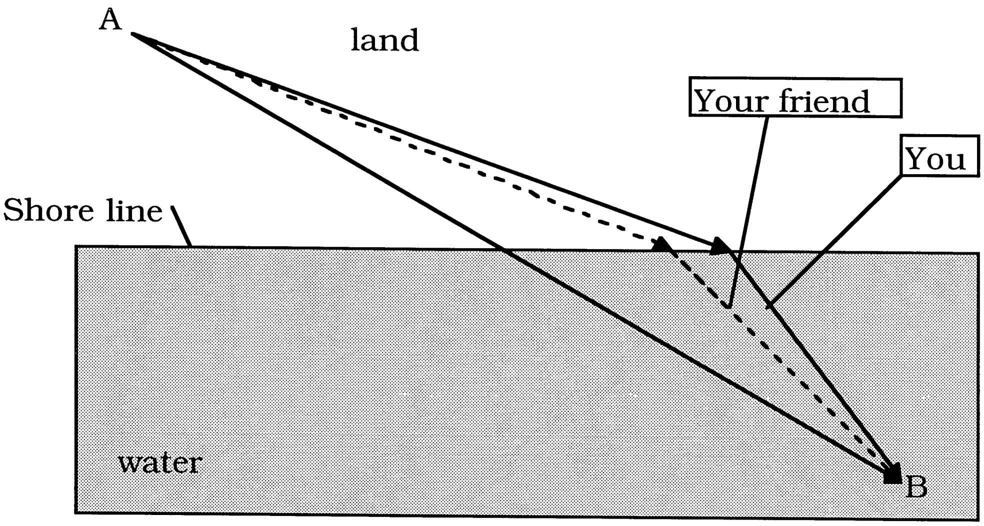
Materials Needed:

1. Metric ruler
2. Calculator
3. Protractor

Discussion:

In 1657, Pierre de Fermat discovered a way to think about the behavior of light called "the Principle of Least Time" or "Fermat's Principle." His idea was this: that out of all possible paths that light might take to get from one point to another, light takes the path which requires the shortest time. (It turns out that this is one of the most powerful ways of formulating the laws of physics - the general approach is called "the Principle of Least Action." These laws, including the laws of quantum mechanics, can all be formulated by considering all possible paths between A and B and finding which path yields the lowest value of a particular quantity.)

An interesting way to introduce this concept is by using the following analogy. Suppose that a person who cannot swim has fallen out of a boat at point B into the water and is screaming for help. Assume that point A is on the shore and the shoreline separates the water from the land. You are at point A on land and see the person fall in the water. You can run and you can swim, but you can run faster than you can swim. What do you do? Do you go in a straight line?

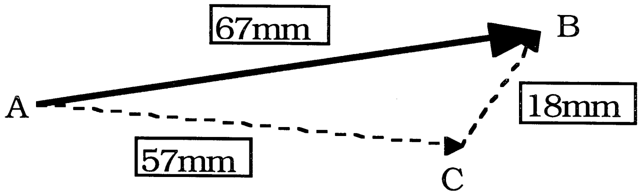


You should realize that it is better to travel a greater distance on land than on the water, because you go so much slower in the water. Therefore your path will not be a straight line, but will be bent as shown by the bent path above. This is an analogy that explains the principle of light refraction.

Now, taking this analogy a bit further, suppose that you and your friend were at point A and observed the person falling in the water at point B. You both run at the same speed, but your friend swims a lot faster than you. How will his path differ from yours?

You should realize that it will be advantageous for your friend to swim a longer distance in the water than you because your friend is a faster swimmer than you. Therefore your friend's path will be different from yours, and will not be as bent as yours. This is an analogy that explains the principle of light dispersion and explains why a prism splits light into the rainbow of colors.

Now let's consider two points A and B.



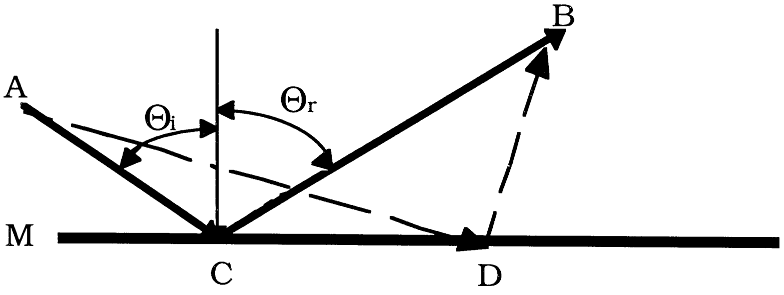
	Straight solid line path	Dashed line path
x (mm)	67	57 + 18 = 75
t=x/v	67mm/v	75mm/v

Fermat's Principle says that the way to get from A to B in the shortest time is to go straight from A to B. Therefore, in the same medium, light travels in a straight line. Any other path, such as the dashed path will be longer, so that it would take the light a longer time to travel from A to C to B, since it's speed doesn't change along the different paths. The table above shows the distance x of each path in mm and the time it would take light to travel from A to B along each path. This time is determined using the equation x=vt or t=x/v, where x is the distance that light travels, v is the speed of light, and t is the time that it takes for light to travel the distance x.

Student Exercise 1:

Draw 2 points A and B on a piece of paper. Draw a straight line path connecting A and B and measure the length of the path. Now, using 2 or 3 straight line segments, draw other paths that go from A to B and measure each of their lengths. As in the table above, calculate the time it takes for light to go from A to B along each of the different paths, using the equation t=x/v. Which path length produces the shortest time and why?

Now suppose that we add a mirrored surface M and ask the question: what is the way to get from A to B in the shortest time, where the light has to strike the mirror?



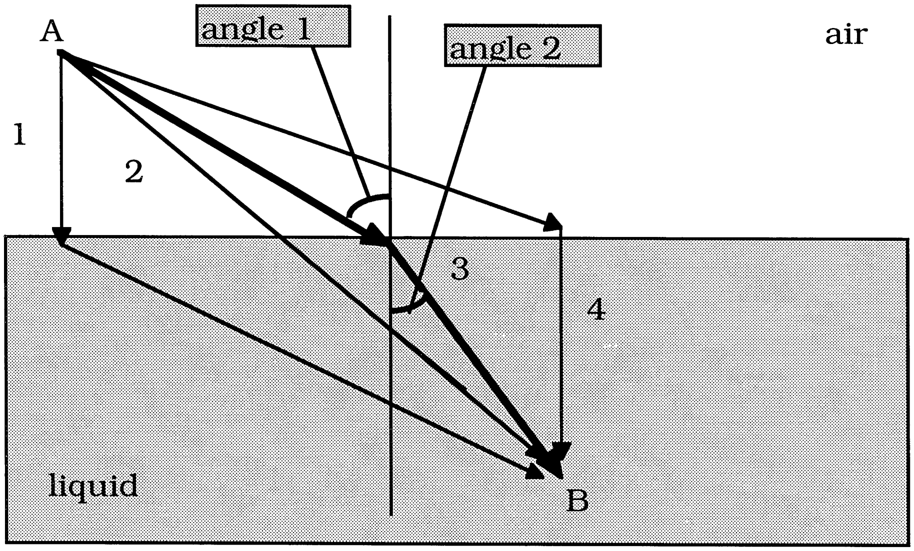
	Solid path (ACB) ($\Theta_i = \Theta_r$)	Dashed path (ADB)
x (mm)	30 + 53 = 83	63 + 30 = 93
t = x/v	83mm/v	93mm/v

It can be shown by geometrical arguments or by trial and error that the light will travel the path shown as ACB, where $\Theta_i = \Theta_r$. This can be demonstrated by measuring the distances of other paths, such as the dashed line path as shown in the table above: they will all be longer than the solid line path shown. Therefore, the time it takes light to travel from A to the mirror to B will be shortest for the solid line path shown. In other words, when light is reflected, the angle of incidence Θ_i = the angle of reflection Θ_r, because that leads to the shortest time for light to travel from A to the mirror and then on to B.

Student Exercise 2:

Draw 2 points A and B on a piece of paper above a line, as shown in the reflection example above. Using a protractor, draw a straight line path that goes from A to the line (representing the mirror) and then to B, where the angle of incidence of the first line equals the angle of reflection of the second line. Measure the length of the path. Now, using 2 other straight line segments, draw another 2 paths that go from A to the line (representing the mirror) to B and measure each of their lengths. As in the table above, calculate the time it takes for light to go from A to B along each of the different paths, using the equation t=x/v. Which path length produces the shortest time and why?

Now we consider the situation where light travels from A to B, but A is in air and B is in a liquid, as shown in the diagram below.



We will assume that the speed of light in the liquid is lower than that in air by a factor of 1.47. (Note to teacher: This index of refraction was used because it satisfies Snell's Law in the exact example drawn above. You could make up your own example: just be sure to make the angles of the path of least time satisfy Snell's Law.)

Student Exercise 3:

Determine which path light will take to minimize the time it takes to travel from A to B by calculating the time it takes for light to travel each of the 4 different paths shown in the example above. Assume that n=1.47, in other words that the speed of light in the liquid is a 1.47 times slower than that in air:

v liquid = v air/1.47.

Use the equation t=x/v, where t is the time it takes light to travel a distance x at a speed v.

What does this indicate about the behavior of light as it enters a medium of different density?

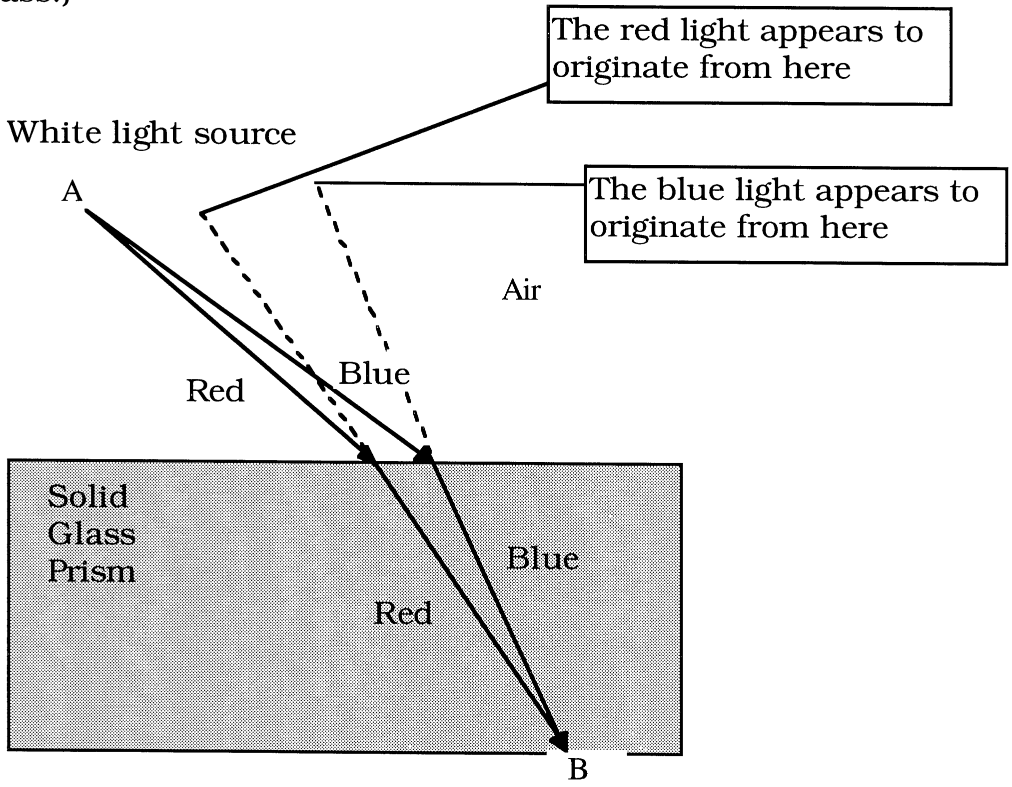
Measure the angle of incidence and the angle of refraction of the path that takes the shortest time. When light goes from air to this liquid along the path of shortest time, what is the relationship between the angle of incidence and the angle of refraction? (Hint: Consider the sine of the angles.)

Student Exercise 4:

Shine a laser light beam from a laser pen through a glass of water or a solid transparent object. Record and explain why the laser light takes the path it does before it enters the water/object, at the interface and in the water/object.

The Prism

The Principle of Least Time allow us to understand how a prism reveals the rainbow of colors present in what seems to be white light. Again, we must make an additional assumption here. We must assume that the index of refraction n of a material depends on the wavelength (or color) of the light. The shorter wavelength blue light has a higher index of refraction n than longer wavelength red light. For glass, the index of refraction of blue light is about 1.54, while the index of refraction of red light is about 1.50. This means that blue light travels slower in glass than red light. This is similar to the analogy of the two friends rescuing the fallen person described above. As in that analogy, the path of the faster swimmer in the water (the faster red light in the glass) is less bent than for the slower swimmer (the slower blue light in the glass.)

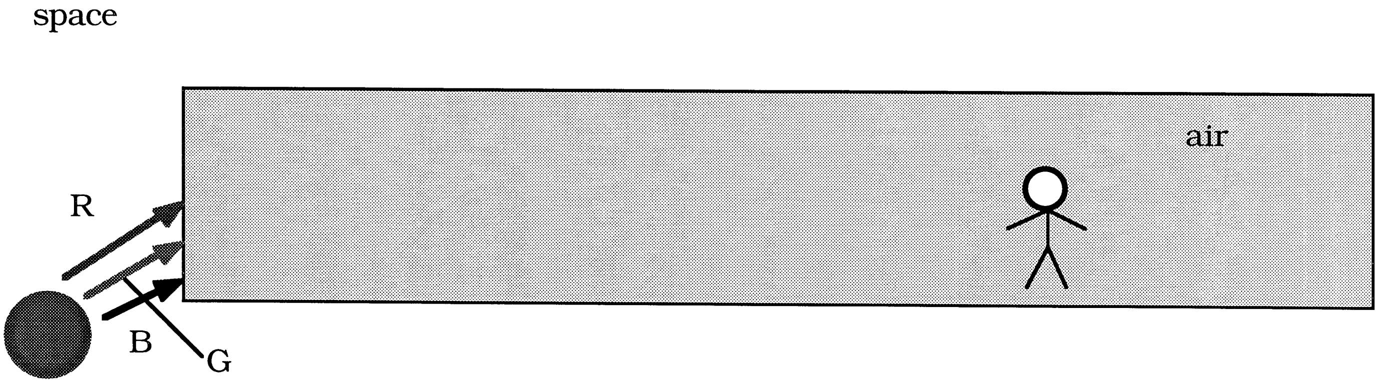


Note that to an observer at point B, the red and the blue light appear to originate from different places, so that the colors appear to be spread out. In other words, the prism has split the white light into the familiar rainbow of colors. The blue light exhibits the greatest dispersion. In other words, the blue light is bent more from its original direction than the red light is bent from its original direction.

Student Exercise 5:

Recall (in the answer to question 5 in laboratory 1-2-2) that the blue light is preferentially scattered by the atmosphere leading to red or orange sunsets. We just learned above that blue light exhibits greater dispersion than red light, as it enters a medium with an index of refraction of n=147. In general, blue light exhibits greater dispersion than red light as it enters a denser medium. In general, the shorter the wavelength, the greater the dispersion: blue light exhibits greater dispersion that green light which exhibits greater dispersion than red light.

Predict what we will see in the situation presented below, as the sun just sets below the horizon. Explain why this produces a green flash.



Answers:

1. The straight line path from A to B takes the shortest time and is the shortest in length. This is because light follow the Principle of Least Time.

2. The path where the angle of incidence of incidence equals the angle of reflection takes light the shortest time to go from A to B. This is because light follows the Principle of Least Time.

3.

	Path 1	Path 2	Path 3	Path 4
x air (mm)	25	38	49	70
x liquid (mm)	73	49	40	32
t air	25mm/(v air)	38mm/(v air)	49mm/(v air)	70mm/(v air)
t liquid	73mm/(v liq)= 107mm/(v air)	49mm/(v liq)= 72mm/(v air)	40mm/(v liq)= 59mm/(v air)	32mm/(v liq)= 47mm/(v air)
t total = t air + t liquid	132mm/(v air)	110mm/(v air)	108mm/(v air)	117mm/(v air)

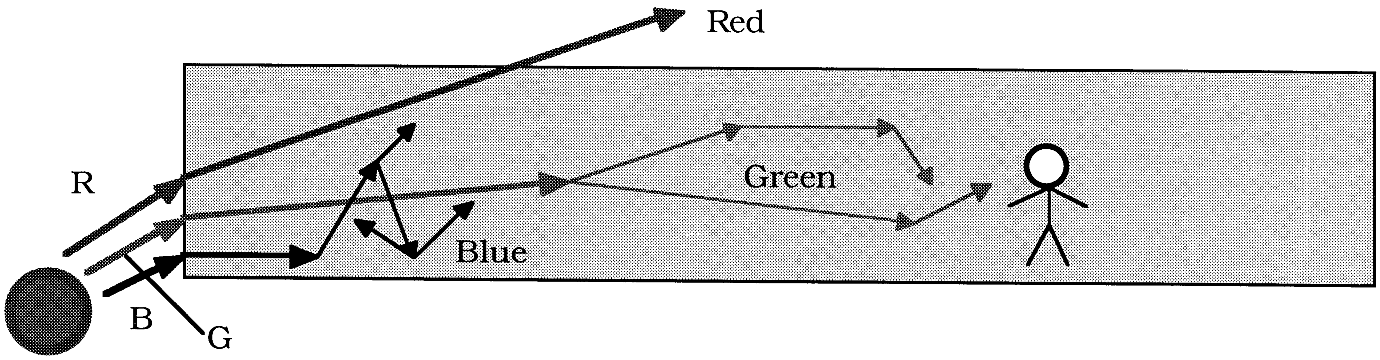
Path 3 is the one that requires the least time to travel from A to B. Therefore the light will bend or refract as it enters a medium of different density.

Path 3 satisfies Snell's Law:

sin(angle 1) = n sin (angle 2), where n=1.47.

4. The light travels in a straight line in the air. It then bends as it enters the water/object, because it travels slower in the water/object than in air. This again verifies that light will bend towards the normal direction when it enters a medium with a higher density.

5. The blue light is scattered away from the observer, because the light must traverse a very long length of atmosphere as the sun is setting. Note that the blue light exhibits the largest amount of dispersion (bending). The red light is hardly scattered at all, so it passes easily through the atmosphere. It is bent less than the blue or green light, so that it passes above us. The green light is just scattered a little, so much of the green remains. The green light is bent more than the red light, so at this orientation, which only occurs for a brief period of time, it is the only light that we see. Hence, it is called the "Green Flash."



2. Color in Gases

Matter can exist in three different states: gaseous, liquid, and solid. At room temperature and atmospheric pressure most common gases have a relatively simple molecular structure. For example, oxygen and nitrogen are diatomic molecules that have no absorption bands in the visible spectrum and are therefore colorless.

Air is a mixture of gases that is composed of mostly nitrogen and oxygen with small amounts of argon, neon, helium, krypton, xenon, carbon dioxide, hydrogen, and water vapor. The atmosphere is confined to the earth by gravity and with diminishing density and pressure extends to an altitude of approximately 75 km. If nitrogen and oxygen have no absorption bands in the visible spectrum and are colorless, then why is the sky blue? It could be due to one of the other constituent gases, but this is not the case, because they are all colorless also. Color in gases, especially in a large body of gases such as the earth's atmosphere, can be caused by physical effects. These include Rayleigh scattering due to small particles and density fluctuations in the atmosphere, and Mie scattering due to larger particles in the atmosphere. These phenomena are responsible for the blue sky and red sun sets and will be demonstrated in a simple experiment. Refraction also contributes to atmospheric color effects.

Some gases are colored due to absorption bands in the visible spectrum, such as chlorine (green), bromine (brown), and oxides or nitrogen (yellow and reddish brown). These are chemical causes of color, because the photons interact directly with the electronic structure of the substance. We will investigate how oxides of nitrogen behave and show that they are responsible for the color of smog. Clouds are made of water vapor and droplets and are white or gray. This is due to scattering, not to absorption of light.

At high temperatures even solids can vaporize and form gaseous species. When large metallic atoms with more complex electronic structures are vaporized and excited, a wide range of electronic excitations is possible. One set of experiments examines how metals can be vaporized in a flame to create a wide range of colors. Emergency flares, sky rockets, and other pyrotechnics take advantage of these phenomena to create bright signals or spectacular night time displays.

Chromatics - The Science of Color

Laboratory No. 2-1

Color in Gases - Fireworks and Flame Photometry

Purpose:

To investigate the behavior of metals in a flame and determine the flame emission colors produced by a variety of metals.

Materials:

1. Bunsen burner
2. Nichrome or steel wire
3. Lithium chloride, sodium chloride, potassium chloride, calcium chloride, strontium chloride, barium chloride, thallium chloride, boric acid, copper chloride, lead chloride. Chlorides work the best, but other salts, such as nitrates, can be substituted.

Discussion

A flame has sufficiently high temperature to dissociate many salts and form a large population of atoms or molecules. The flame temperature is sufficient to excite a fraction of electrons in these atoms into higher electronic states. Electrons in the excited states can return to the ground state by emission of photons with very specific energies or wavelengths. The energy of these photons is characteristic of the excited and ground states of the electrons in an atom and therefore is indicative of the element. These emission lines can be used to quantitatively and qualitatively determine which elements are present.

Emission lines and colors for some elements are provided in table 1.

Table 1: Emission lines and color for some of the elements.

Element	Emission Lines (nm)	Color
lithium	610, 671	deep red
sodium	589	yellow
potassium	405	violet
calcium	423, 559, 616	orange red
strontium	408, 461, 606, 687	crimson red
barium	487, 514, 543, 553, 578	yellow green
thallium	535	green
boron, borates	broad bands	green
arsenic, antimony, bismuth, copper, lead	broad bands	blue

Sharp emission lines are produced when a large population of excited atoms exist in the flame. Molecular species such as a OH radicals, CN radicals and C molecules are also frequently present in flames. In addition some metals form stable oxides which are not reduced to atomic species. These molecules are responsible for broad emission bands in the spectra of flames which are superimposed on the sharp emission lines of the metallic atoms.

Safety:

1. Wear safety glasses as sparks may occur.
2. The flame and hot wire must be handled very carefully.
3. Do not inhale vapors emitted by the flame or burning of salts

Procedure:

1. Use a colorless gas flame such a Bunsen burner.
2. Cut a new 25 cm piece of steel or nichrome wire and clean in the gas flame.
3. Dip the wire in metal salt and place in flame.
4. Observe color of flame.
5. Repeat steps 1-4 for all salts provided, after cutting the used end off.

Questions:

1. What form are the metal salts in when they are in the flame?

2. What causes the metal atoms to emit light?

3. Why do different metals emit different colors of light?

4. Why are some flame spectra narrow emission lines and others are broad bands?

5. How do pyrotechnic displays (e.g. sky rockets) obtain their color?

Answers:

1. The metal salts are dissociated by the temperature of the flame and form free atoms of the metal.

2. The metal atoms are promoted to an excited state by the temperature of the flame, which causes an electronic transition to a higher energy state. The metal atoms in the excited state emit a photon of light when they return to the ground state. The energy of this emitted photon determines the color that is observed.

3. The energy of the emitted photon, and therefore the color of the light, depends on the energy difference between the excited and the ground electronic state of the metal. Every element has a unique electronic configuration, therefore each metal has a unique excited and ground state.

4. Sharp lines occur when the emission is from atomic species with a specific electronic transitions between the excited and ground states. Broad bands occur when the emission is from molecular species, which have a broader range of energies between the ground and excited states.

5. Metal salts are added to the explosive charge of the pyrotechnics. By varying the species, the concentration, and the location of the metal salt a wide variety of colors and effects can be achieved.

Chromatics - The Science of Color

Laboratory No. 2-2

Color in Gases - Smoggy Air

Purpose:

To investigate the formation of oxides of nitrogen and how they affect the color of air.

Materials:

1. Erlenmeyer flasks
2. Glass tubing
3. O.1 M nitric acid
4. Copper metal (powder, wire, shot, or shavings)
5. Ice
6. Spectrophotometer (optional)

Discussion:

Nitrogen is a colorless gas which makes up 78 % by volume of the atmosphere. Nitrogen forms several oxides under proper conditions. Nitrous oxide, N_2O, is a colorless, odorless gas, known as "laughing gas," and is often used by dentists as a general anesthetic. We will not be dealing with nitrous oxide in this experiment.

Nitric oxide, NO, is a colorless gas that can be prepared from nitrogen and oxygen at high temperature. During thunderstorms NO is formed when lightning passes through the air. NO is also formed in automobile engines and exhausted into the atmosphere. In the laboratory NO can be prepared by the oxidation of copper by nitric acid:

$$3\ Cu + 8\ HNO_3 \rightarrow 2\ NO + 3\ Cu(NO_3)_2 + 4\ H_2O$$

Nitric oxide, NO, is a reactive gas, which reacts with oxygen to form nitrogen dioxide by the following equation:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

Nitrogen dioxide, NO_2, is a reddish-brown gas that dimerizes to form dinitrogen tetroxide by an exothermic reaction:

$$2\ NO_2 \leftrightarrow N_2O_4 + \text{heat}$$

Dinitrogen tetroxide, N_2O_4, is a slightly yellowish gas. An increase in temperature drives the equilibrium toward the nitrogen dioxide, NO_2, and results in a darker color. NO_2 absorbs light which leads to further reactions in the formation of photochemical smog. Therefore the brownish color associated with smoggy air is more of a problem in warm climates, such as Los Angeles and Mexico City, than in cold climates. There are other oxides of nitrogen which will not be discussed in this experiment.

The ground state and the first excited electronic state of Nitrogen dioxide, NO_2, are separated by an absorption band centered at ~430 nm. This is a diffuse absorption band in the blue spectral region at room temperature. The complement of this blue absorption is the appearance of a reddish-brown color.

Safety:

1. Perform experiments in a fume hood and do not inhale gases evolved.

Procedure:

1. Assemble gas evolution apparatus in a fume hood.
2. Place ~50 mL of ~0.1 M HNO_3 in a 250 mL flask.
3. Add ~2 g of copper metal in the same flask and insert one hole stopper.
4. Place 100 mL Erlenmeyer or volumetric flask in beaker with ice water.
5. Insert other end of line in 100 mL Erlenmeyer or volumetric flask.
6. Collect gas in flask.
7. Observe color of gas.
8. Remove flask from beaker with ice water and allow to warm to room temperature.
9. Observe color of gas.
10. Place flask back in ice water and observe color of gas.
11. If available transfer some of the gas to a long-path-length cuvette and obtain the absorption spectrum in a spectrometer.

Questions:

1. What molecular species is responsible for the brown color of smoggy air?

2. At what wavelength does the absorption occur?

3. How do oxides of nitrogen form in modern cities?

4. Why did the color of the gas change when it warmed to room temperature? How does this relate to the intensity of smog on a warm summer day compared to a cold winter day?

Answers:

1. The brown color of smoggy air is due the presence of nitrogen dioxide, NO_2, which is a reddish-brown gas, and to a lesser extent dinitrogen tetroxide, N_2O_4, which is a slightly yellowish gas.

2. The absorption band of nitrogen dioxide occurs at ~430 nm, which is in the blue region of the spectrum. If the absorption is in the blue region, the transmitted light, or the complement, is reddish. Due to the diffuse nature of the absorption band, the color appears reddish brown.

3. Oxides of nitrogen form in the combustion process of fossil fuels where the nitrogen in air is oxidized along with the fuel.

4. An increase in temperature drives the equilibrium toward the nitrogen dioxide, NO_2, and results in a darker color.

Chromatics - The Science of Color

Laboratory No. 2-3

Color in Gases - Rainbows

Purpose:

To study and understand the concept of refraction by discussing how a rainbow is formed and simulating it with an experiment.

Materials:

1. A glass or plastic prism
2. mm slide projector
3. Glass beaker
4. Reflective foil or aluminized mylar
5. Round bottom glass flask (optional)
6. Large cardboard box (eg. Computer box)

Discussion:

A straw in a glass of water appears bent (try it). A fish in the ocean will appear displaced and closer to the surface than it actually is. If you were a spear fisherman looking for dinner, it would be important to understand the physics involved so that you speared the real fish rather than the "virtual" fish. This effect is illustrated in Figure 1. The important mechanism involved is called refraction and is due to the fact that light travels slower in water than it does in air or vacuum. The light wave slows down and turns (see the discussion of Fermat's Principle of Least Time) as it goes from air to water, causing us to see a displaced image since the brain is conditioned to expect light waves to go in straight lines.

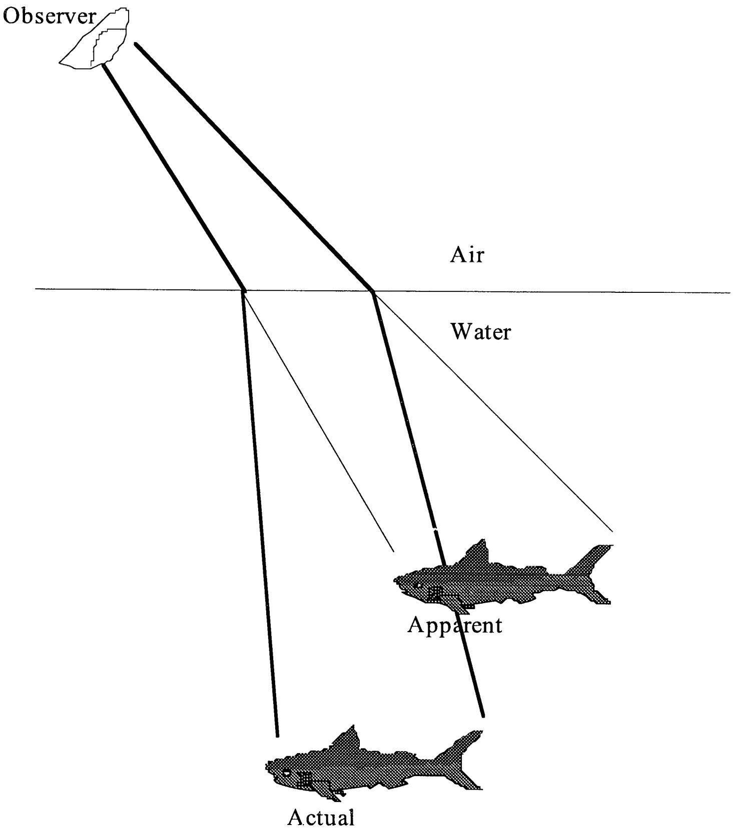


Figure 1: Effect of the Index of Refraction of Water on the Apparent Position of an Object

The refractive index of a material tells us how much it will bend light, or equivalently, the relative speed of light in the medium. The refractive index varies with wavelength so that each wavelength is bent a different amount. You may want to review the discussion in the section on Fermat's Principle, which discusses this in more detail. Red has the longest wavelength of the visible spectrum and is bent the least; violet has the shortest wavelength and is bent the most. A prism separates or disperses white light into a continuous spectrum in the familiar sequence red, orange, yellow, green, blue, indigo, and violet (recall Roy G. Biv). This sequence results from the variation of the index of refraction over the visible wavelength range.

Using a setup like that illustrated in Figure 2, use the collimated light, formed by passing the light from a 35 mm slide projector through a series of narrow slits, to disperse light into its spectrum with a prism. The figure shows a beaker of water rather than a prism. The reason for this will become apparent later. Place the prism a few inches from the slit in the back wall of the box. Move the prism around and rotate it until you see the spectrum on the sidewall of the box. Covering the walls of the box with white posterboard helps give a stronger contrast in the spectrum and truer colors. Trace the light path from the slit in the box through the prism to the spectrum on the side wall of the box. Note the location of colors in the spectrum. What does this tell you about the relative speed of the various colors (wavelengths) of light in the prism and in air?

It is very important to use the two slits shown in Figure 2 to obtain well collimated light for this experiment. Issac Newton, in his original experiment, used sunlight through a slit on a window. You can duplicate this with Venetian blinds when the angular relationships are just right. Since the sun is 93,000,000 miles away its light rays are very parallel (collimated) by the time they reach the Earth. However, light from a nearby incandescent light source is quite omnidirectional and must be collimated to produce a spectrum. A very intense light source such as that from the slide projector is necessary to ensure that the intensity of the collimated beam is sufficient to produce a clearly visible spectrum.

Simulation of a Rainbow

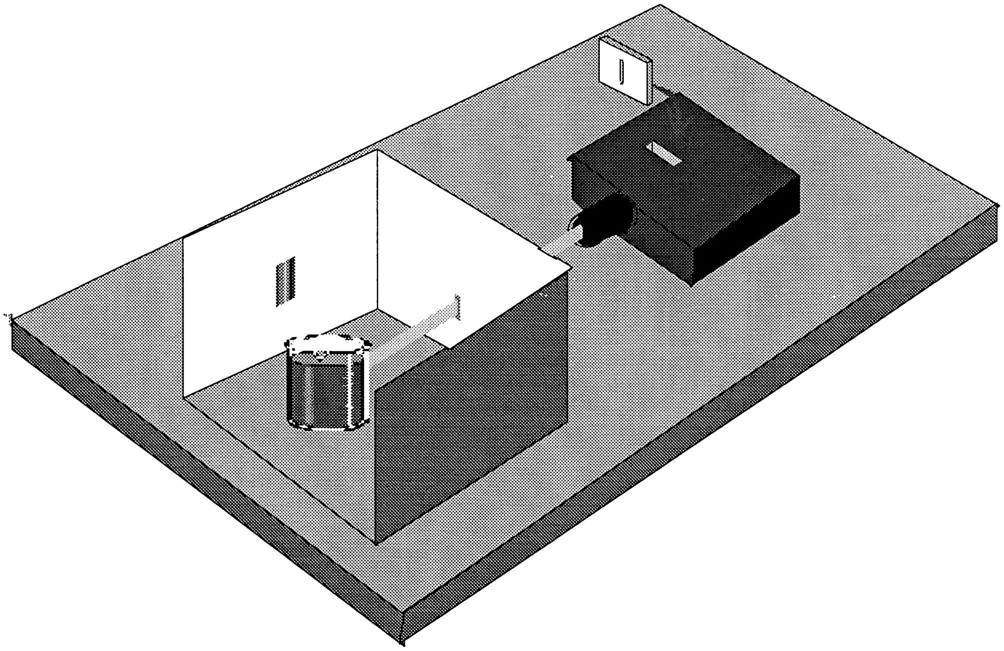


Figure 2: Experimental setup for simulation of a rainbow

One of the most familiar and striking examples of refraction is the appearance of a rainbow after a storm. Individual raindrops act as prisms and bend sunlight in such a way that we see a rainbow. What conditions are required for this to occur? First, we need raindrops on the horizon in front of us, and next, the sun must be shining behind us. Sunlight enters a raindrop, is refracted and reflects off the back surface of the raindrop. As the light exits the raindrop, it is refracted again as shown in Figure 3.

The French mathematician Descartes first figured out in 1637 how a rainbow is produced by directing sunlight onto a large glass sphere. He noted that the location of a given color is always at a fixed angle with respect to the sun, the back of the sphere and the eye of the observer. Red light can be found at an angle of approximately 42° while violet can be seen at an angle of 40° as shown in Figure 4. Since our eyes are at a fixed height, this implies that at any given moment a raindrop delivers only one color to our eyes. As the raindrop falls, the color of light able to reach our eyes changes so that all the colors of the rainbow will reach us from a given raindrop, but not at the same time! The full rainbow is created from a composite of many raindrops, all contributing one color at a time. If there are multiple observers, no two people will see the exact same rainbow at the same time! From Figures 3 and 4, we can see why red is at the top of the rainbow and violet at the bottom.

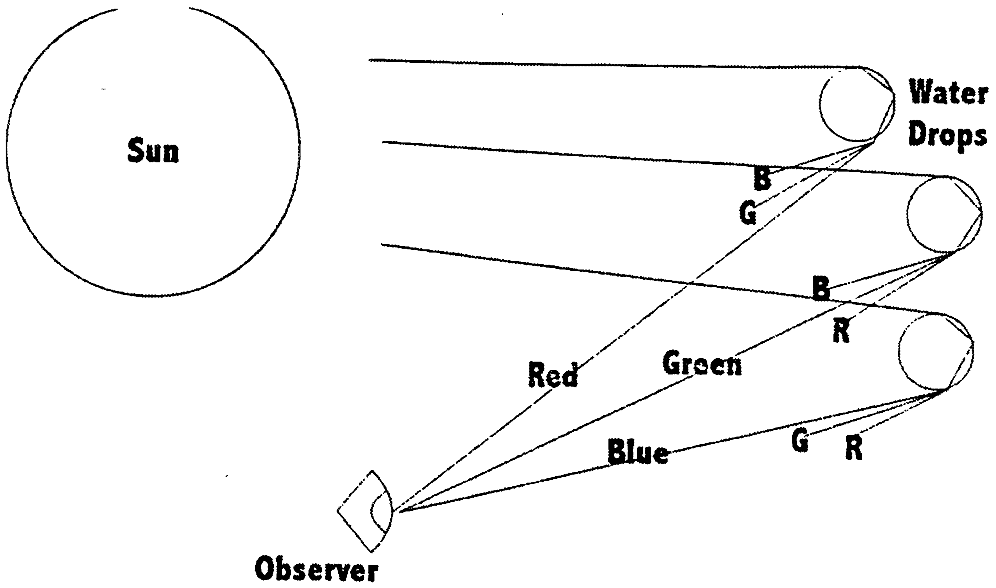


Figure 3. Rainbows are produced by refraction of sunlight in raindrops.

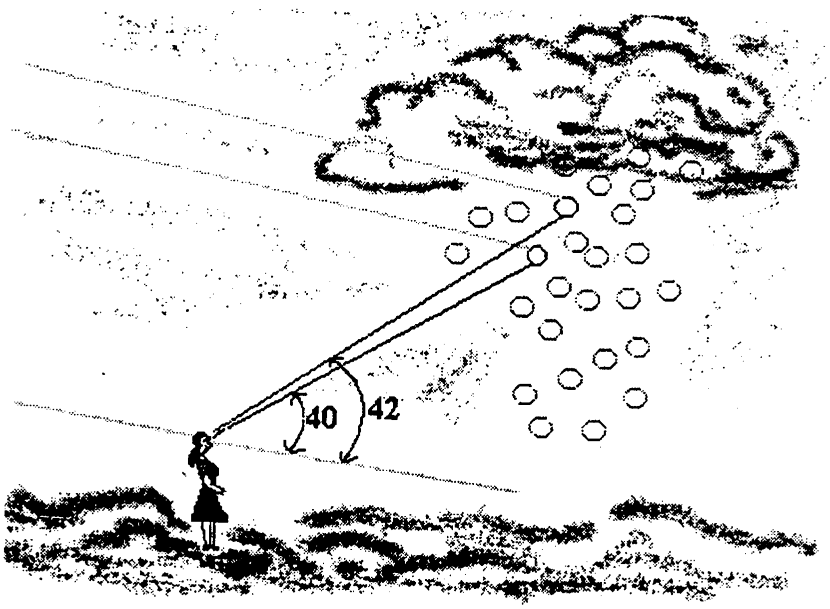


Figure 4. Red light emerges at an angle of 42° from a raindrop while violet light emerges at 40°.

Thanks to Beverly Lynds for the use of her drawings (Figures 4 and 5) depicting how a rainbow is formed. For further information about rainbows, check out her site at http:/twww.unidata.ucar.edutstafflblynds/rnbw.htrnl.

The 42° angle is a measure of the *deviation* of the incident and emergent rays and is calculated as 180° - 42° or 138° from the direction of the light source. This is the minimum deviation of all visible light rays incident on a raindrop. Rotating this image about the line of the light rays from the source (from the sun to the anti-solar point) shows how the familiar bow shape arises, as depicted in Figure 5a. We can see the entire circle of rainbow if we are high enough, such as in an airplane above the clouds, or if we walk into a rainbow produced by the spray of a hose.

Occasionally, if the sun is bright and the sky dark, we may see another, fainter or *secondary* rainbow above the *primary* one. Since light reflects off the inside surface of the raindrop twice to produce the secondary rainbow, it is fainter than the primary rainbow and the colors are reversed! The red and violet rays emerge from the raindrop at 52° and 54.5°, respectively. This is illustrated in Fig. 5b.

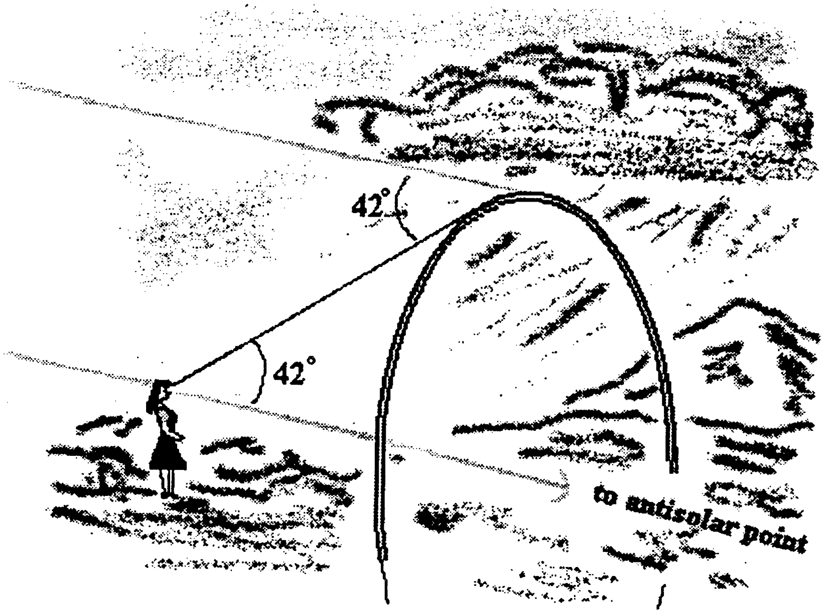


Figure 5a. The arc of a rainbow is produced by the angular limitations of light that has been refracted twice and reflected once in a raindrop.

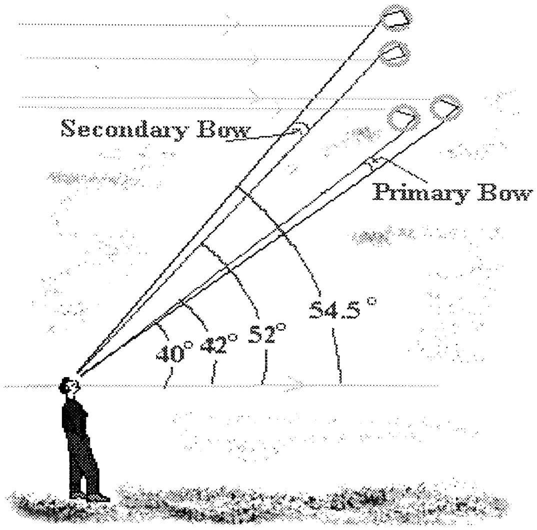


Figure 5b: The secondary rainbow is produced by an additional reflection in each raindrop.

The conditions for observing a rainbow are having the sun relatively low in the sky at the back of the observer and rain clouds in the distance in front of the observer. The distances and angles must be such that the included angle meets the 40 to 42 degree requirement. This can be verified by using a fine misting nozzle on a hose on a sunny day.

Procedure:

1) Prepare an experimental setup as illustrated in Figure 2. Start with a cylindrical beaker as shown. Place the beaker about 12 inches from the slit in the box and so that the slit of light hits the beaker well off its centerline. Adjust the beaker until the rainbow is visible on the sidewall of the box. The use of white posterboard will enhance the intensity and color of the rainbow.

2) Place some reflective tape or foil on the beaker where the light impinges its back wall. This will intensify the rainbow by reflecting more of the incident light into it.

3) Put a drop of milk in the beaker of water and trace the path of the light from the slit through the beaker and to the visible rainbow. Measure the angles of reflection and refraction. Milk forms a very fine emulsion of droplets in the water. Scattering of the light by the droplets makes the light beam visible in the water. Similarly in dim light, scattering of light from particles in the air such as dust often makes the light path in air visible.

4) Repeat the experiment with a spherical flask.

5) Compare the light paths for the cylindrical and spherical beakers.

Questions:

1. Recall that a prism separates white light into its constituent colors, bending violet the most and red the least. What can you say about the relative indices of refraction for these two wavelengths in the prism?
2. Plexiglas and quartz have different indices of refraction with that of quartz being somewhat higher. Would you expect the color dispersion to be different using prisms made of the two materials? What characteristic would you look for in a material to make prisms out of?
3. Diamond has the highest index of refraction of any common material. Can you suggest how this might relate to the very high value put on diamond as a gem stone?
4. Why does the beaker need to be off center relative to the incident light beam? Follow the light path for the case when the beaker is perfectly

centered. Why can a bird that is hovering directly over a fish catch it every time, while an observer seeing it from a side angle needs to make a correction for the actual as opposed to the virtual position of the fish?

5. Can a rainbow be made with moonlight?
6. Why is the order of the colors reversed in a double rainbow? Draw an illustration tracing the light rays from the source through the raindrops to the observer.

Answers:

1. The index of refraction for red light is smaller than that for violet light in quartz.
2. The higher the index of refraction the greater the dispersion of color in the resulting spectrum. The highest index of refraction materials make the best prisms.
3. The very high index of refraction of diamond produces a high degree of color dispersion which results in the highly prized brilliance and sparkle of the diamond.
4. According to Fermat's Principle the light beam will only be bent at an interface between two materials with differing indices of refractionwhen it enters at other than normal incidence. This is because there is no path other than a straight line that will reduce the time of travel of the light ray at normal incidence. The light beam is still slowed down, but it is not deflected. The magnitude of the refraction increases as the angle of incidence of the beam increases. This can be observed with the milky water. The amount of color dispersion in the rainbow also increases. The bird directly overhead sees the fish at normal incidence and doesn't have to make a correction for its position.
5. Yes-it will be faint, but recall that moonlight is reflected sunlight. The moon is far enough away to produce very well collimated light on the Earth.
6. To create a double rainbow, the light is reflected twice inside a raindrop. The second reflection causes the colors to emerge in reverse order (refer to figure 5b).

Chromatics - The Science of Color

Laboratory No. 2-4

Color in Gases - Blue Sky and Atmospherics

Purpose:

This section addresses the nature and cause of color phenomena observed in the atmosphere; including blue sky, sunsets, and clouds. A simple experiment that simulates the blue sky and red sunset phenomena is described.

Materials:

1. Ring stand and clamps
2. Tall beaker or cylinder
3. A few drops of milk
4. A collimated light source
5. A three sided enclosure with white walls (optional)

Discussion:

One of the classic questions that is often asked but not generally understood even by educated adults is; why is the sky blue? The reason it turns out is the same reason that sunsets are red and clouds are white. The fundamental basis of these atmospheric color phenomena is scattering, which results from the interaction of light with small particles (smaller than the wavelength of light), droplets, and molecules in the atmosphere. There are two general classes of scattering: Rayleigh Scattering, which is caused by particles and molecules smaller than the wavelength of light and Mie Scattering, which results from larger particles such as water droplets or dust. Rayleigh Scattering is a very weak scattering effect; however, since the path length of light in the atmosphere is so long the effects are very apparent. In the absence of Rayleigh Scattering the sky would appear black as it does at night or to astronauts in space.

On a clear, dry day there is little in the atmosphere except molecules of nitrogen and oxygen. These molecules have no absorption bands in the visible spectrum and are therefore colorless. However, there is scattering of the shorter wavelength blue light in the atmosphere off small particles and density fluctuations in the atmosphere. The blue light is therefore preferentially scattered in all directions. The sky looks blue and the sun and the sky in the vicinity of the sun appear to be the color of white with blue subtracted out, which is slightly yellow.

As the moisture content (humidity) in the air increases, tiny water droplets are formed that scatter all wavelengths of light equally, producing a whitish cast to the sky. The scattering from these larger particles is referred to as Mie scattering. This is why the sky appears an intense dark blue as observed from a mountain where the atmosphere is dry and cold, and a pale whitish blue in warm, humid areas. For the same reason, clouds, which are regions containing high concentration of microscopic water droplets, appear very white. The relatively intense scattering from their high concentration of tiny water droplets makes the clouds appear as tangible objects. As the water content of clouds gets even higher, as just before a rainstorm, even larger water droplets form and begin to absorb, as well as scatter, light resulting in a gray appearance.

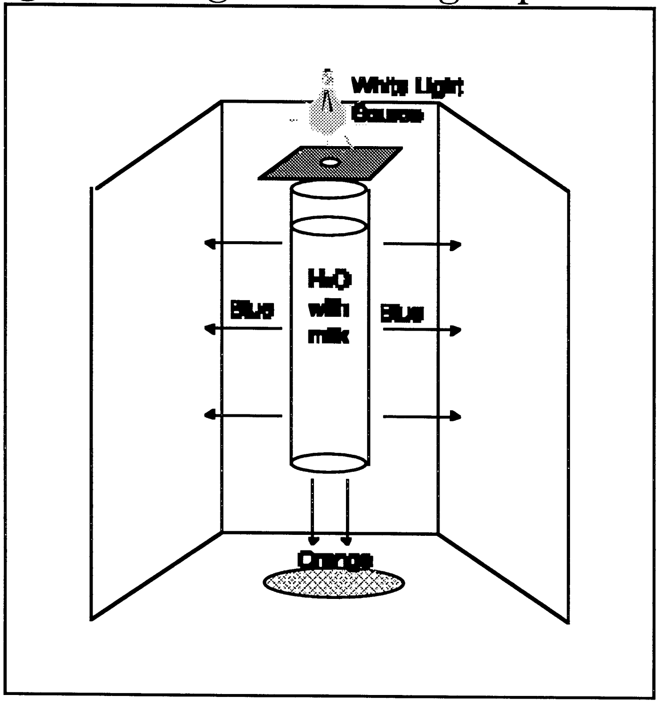
Similar phenomena produce the brightly colored sky and sun observed at sunrise or sunset. As the sun becomes low in the sky, the path length of light through the atmosphere becomes longer, causing blue light to be scattered more strongly. A portion of the blue light is scattered away from the observer so that the longer wavelengths of light (toward the red end of the spectrum) are preferentially seen by the observer. As the sun gets low in the sky the observer first sees orange; and then as the sun gets lower and lower and blue light is even more effectively scattered he sees red and then violet. The light is also scattered by clouds so they also appear orange, red or violet. Sunsets are enhanced by the presence of high concentrations of very small particulates in the atmosphere, as was observed after major volcanic eruptions such as Mt. Pinatubo and Mt. St. Helens.

Another atmospheric effect that is known to residents of coastal regions is the rarely seen "Green Flash", which is the green coloration above the sun just as it disappears below the horizon. The "Green Flash" may also be observed at sunrise. This effect was noted in a 1881 novel of that name by Jules Verne. The Green Flash is a refraction effect caused by the atmospheric density gradient which act much like a prism in bending the green, blue and violet rays toward the observer, while the red, orange and yellow rays illuminate the sky above him. Most of the violet and blue light is removed by scattering and the observer momentarily sees green, just as the sun sets completely. This is illustrated schematically in the answer to question 5 in Laboratory 1-4.

Procedure:

The effect of Rayleigh Scattering in producing scattered blue light can be readily demonstrated in the laboratory as can the enhanced transmission of red/orange light. The experimental setup is illustrated in Figure 2.4.1. The setup consists of a strong collimated light source that is directed through a column of water. With pure water, the transmitted light is unchanged from the color of the source. However, when a few drops of milk are added to the water to produce scattering centers, pale blue light can be observed perpendicular to the light source; and the observed transmitted beam is shifted to the orange portion of the spectrum. These effects can be observed best if a partial enclosure with white walls is placed around the experiment and the room is darkened.

Fig. 2.4.1: Light Scattering Experiment



Questions:

1. Why does snow have a white color where water and ice are colorless?

2. What color does the Moon's sky appear to an astronaut standing on its surface?

3. What color would the Earth's oceans appear to be to this same astronaut standing on the surface of the Moon?

4. What happens to the blue sky on an overcast day?

5. Natural light is often referred to as white light, yet the sun appears more yellow than white; why is this?

6. Would ultraviolet light be more or less scattered by the atmosphere than visible light?

7. Why are fog lamps for street lighting or on automobiles yellow rather than white?

Answers:

1. Snow is made up of very small transparent ice crystals and a lot of air. Light is scattered from each of the surfaces between ice crystals and air that it encounters. Since there are so many ice/air interfaces the light is completely scattered and essentially none is transmitted through the snow. Since all wavelengths are scattered equally, the eye sees white light. In the case of liquid water or a dense ice, there are no interfaces to scatter, all wavelengths of light are transmitted and the materials appear colorless.

2. In the absence of an atmosphere, there would be no Rayleigh Scattering and the moon's sky would appear black with visible stars.

3. The Earth's oceans would appear blue as they do on the Earth due to absorption of red light by the water and the complement is blue color.

4. The overcast is caused by water droplets in the lower atmosphere which produce scattering of all wavelengths of light. When the overcast is complete, all light is scattered, none is transmitted, so the blue sky that is still present at higher altitudes cannot be seen. This is what you observe when you climb through the overcast in an airplane.

5. Because of the preferential Rayleigh scattering of blue light, the sun as viewed from the Earth appears more yellow than it would if viewed from outer space where it would appear quite white.

6. Because of its short wavelength, ultraviolet light would interact more strongly than visible light with molecules and submicroscopic particles in the atmosphere and would undergo stronger Rayleigh scattering than visible light. This is fortunate since the portion of UV radiation that is scattered out of the atmosphere doesn't contribute to sunburn. It is also absorbed by the ozone molecules in the upper atmosphere.

7. Yellow light lacks the blue portion of the spectrum that is scattered by the water droplets in the fog. Consequently, yellow light produces less glare (scattered light) than does white light.

3. Color in Liquids

Liquids, like gases are fluids, but liquids have strong intermolecular forces and higher viscosities and are therefore able to dissolve other liquids and solids. The most abundant liquid is water, which is generally considered to be clear and colorless. On close inspection, water has absorption bands in the infrared which extend into the red region of the visible spectrum. The complement of this red absorption is a blue color. This explains why large bodies of clean water, such as lakes and oceans, appear blue. The presence of algae and plants gives some lakes or parts of the ocean the green color. We examine these effects in an experiment that extracts chlorophyll, the active photosynthetic structure of plants and show what its absorption spectrum looks like.

Most common organic liquids, such as alcohols, ketones, and ethers are simple organic molecules. These compounds contain mainly single bonds with occasional double bonds and have electronic absorption bands in the ultraviolet spectral region and appear colorless. As organic molecules become more complex and contain more carbon-carbon double bonds, the absorption bands shift into the visible and the molecules exhibit color. Groups of atoms in a molecule that determine an electronic absorption or emission band are called chromophores or color centers. These chromophores become more intense for molecules that contain alternating single and double bonds, called conjugated systems. Acid-base indicators are conjugated molecules that also undergo structural changes in response to acid. These structural changes can result in dramatic color changes as will be demonstrated in an experiment.

Metal ions in aqueous solution can also display distinct colors and color changes. When these ions are in solution they do not exist as free ions, but rather they attract a number of water molecules around them and form a cluster or metal ion complex. This complex acts like a large molecule with a wide range of electronic transitions. These electronic transitions are responsible for the color of these metal ions in water as will be seen in experiment number 3-3.

When organic molecules acquire excess energy through reactions or other form of stimulation most of them radiate this excess energy as vibrations or heat. But some organic molecules do not produce heat, but rather radiate excess energy as light in an effect called chemiluminescence. Luminol is one such substance that can be oxidized with laundry bleach. It emits a bright blue light when it decays from its excited state, as will be demonstrated in an experiment. Commercially available lightsticks and necklaces take advantage of this phenomena, but use peroxy-oxalate instead of luminol. Inside the plastic tube of the lightstick is a thin-walled glass tube containing hydrogen peroxide. In bending the plastic tube the inner glass tube is broken which allows the reagents to mix and activate the light producing reaction.

Bioluminescence in fireflies and some ocean creatures is a specialized form of chemiluminescence.

Chromatics - The Science of Color

Laboratory No. 3-1

Why Plants are Green
Color in Liquids - Organic Molecules

Purpose:

To investigate why plants are green and determine the absorption spectrum of chlorophyll.

Materials:

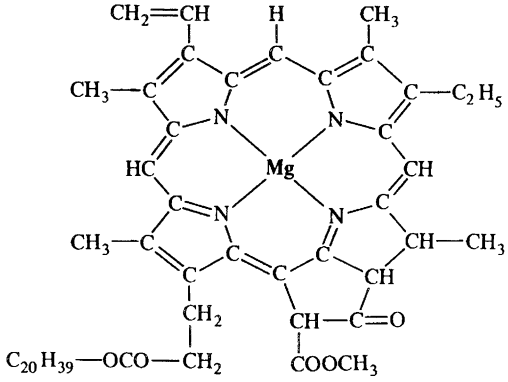
1. Green leaves (grass blades or spinach)
2. Blender (or mortar and pestle
3. Funnel and filter paper
4. Solvents (e.g. acetone, methanol, ethanol, or isopropyl alcohol)
5. Overhead projector, cardboard with slit, and petri dish
6. Diffraction grating
7. Spectrophotometer (optional)

Discussion:

It is the excitation of electrons in atoms and molecules that results in radiation in the visible and UV spectral regions, and hence is responsible for chemically derived color. The energy of the transition and therefore the wavelength, is determined by the nature of the specific atomic groups in the molecule. Atomic groups in a molecule that determine an electronic absorption or emission band are called chromophores or color centers.

Simple organic molecules, containing mainly single bonds, have electronic absorption bands in the UV spectral region and appear colorless. As organic molecules become more complex and contain carbon-carbon double bonds, the absorption bands shift into the visible and the molecules exhibit color. These chromophores become more intense for molecules that contain alternating single and double bonds, known as conjugated systems.

Chlorophyll is a very important biological molecule that is responsible for the conversion of light energy into chemical energy in photosynthetic plants and provides the green pigment of plants. The structure of chlorophyll-a is



The complex molecule contains a ring structure of conjugated single and double bonds with a central metal atom of magnesium. Due to the large absorption of light in the blue and red spectral regions chlorophyll transmits light in the green spectral region.

Sunscreens are an example of commercially available products containing organic molecules with useful absorption properties. Para amino benzoic acid (PABA), oxybenzone, and other active ingredients have very high absorption coefficients in the UV spectral region, but are transparent in the visible. Therefore they effectively block UV and protect the skin from harmful UV radiation, but are colorless and invisible to the eye.

An important pigment used by ancient Egyptians over 4000 years ago is the blue dye indigo. This same dye is used today to provide the color in blue jeans.

Safety:

Normal laboratory safety procedures should be observed.

Procedure:

1. Visually determine color of solvent.
2. Obtain absorption spectrum of solvent with spectrometer. (optional)
3. Place ~50 g of grass or green leaves in blender with ~200 ml of water.
4. Blend until uniformly green.
5. Decant supernatant.

6. Filter supernatant through filter and place in petri dish.
7. Visually determine color of chlorophyll solution.
8. Set up the diffraction grating with the overhead projector as indicated in figure 1.
9. Place the petri dish with the chlorophyll solution as indicated in figure 2.
10. Follow the same procedure as above with cobalt glass, yellow food coloring or yellow plastic disk, green food coloring or green plastic disk, orange food coloring or orange plastic disk, red food coloring or red plastic disk, and blue food coloring or blue plastic disk.
11. Record the results on a data table.
12. Put the chlorophyll in a test tube and place the test tube in front of as strong beam of light (from the overhead projector or a UV light) and record observations.

Alternate Procedure:

1. If blender is not available, place approximately 50 grams of chopped green leaves in mortar.
2. Add a spoon full of sand to help grind up the leaves and break the plant cell walls.
3. Add ~200 ml of organic solvent (ethanol, acetone, methanol, or isopropyl alcohol)
4. Grind the mixture until the liquid is dark green, filter and place the green solution into a petri dish or beaker.

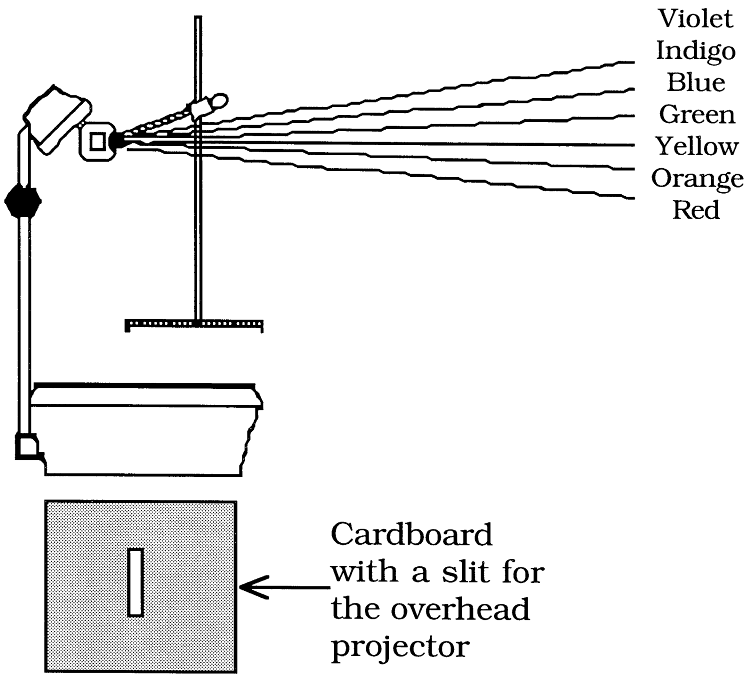


Figure 1

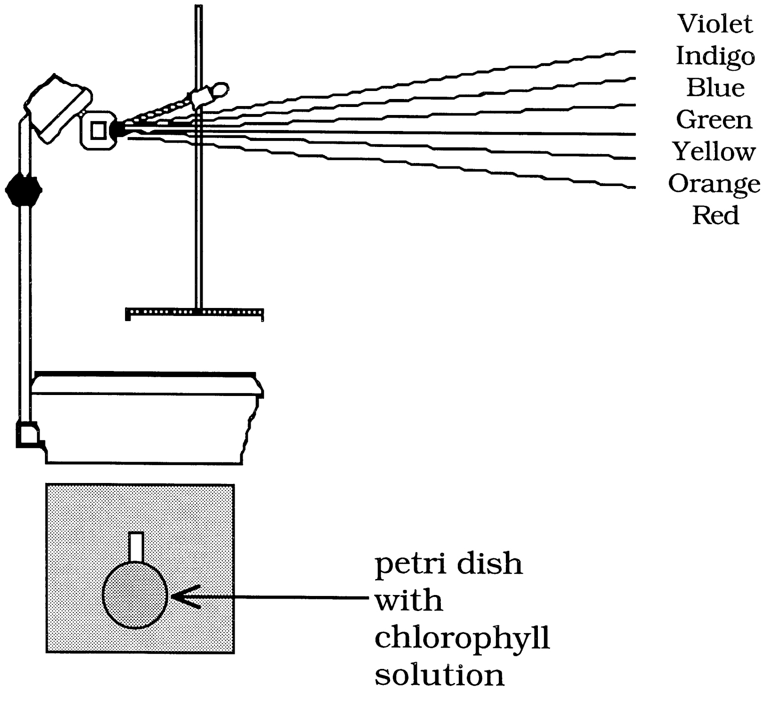


Figure 2

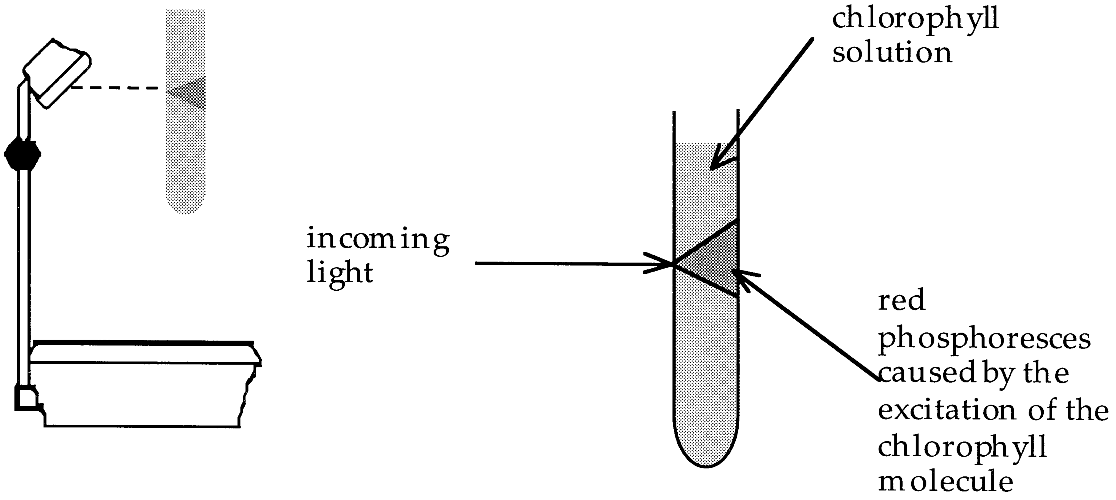


Figure 3

Chlorophyll captures light from the sun and converts its into energy into photosynthesis:

$$6CO_2(g) + 6H_2O(l) \xrightarrow{\text{light,chlorophyll}} C_6H_{12}O_6(aq) + 6O_2(g)$$

By shinning light (or ultra violet light) into a chlorophyll solution, a red color is emitted. This red color is the phosphorescence of the chlorophyll molecule caused by the excitation of electrons in chlorophyll. See figure 3.

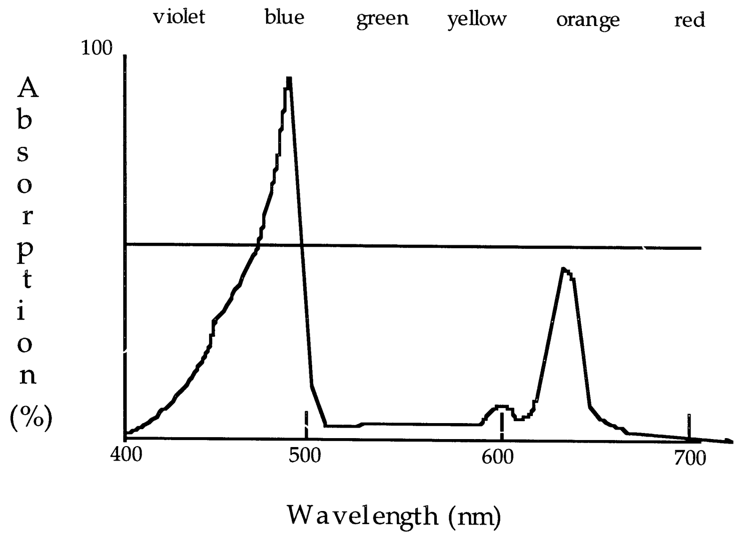


Figure 4: The optical absorption spectra of chlorophyll as a plot of percentage absorption against wavelength.

Questions

1. What type of transition in atoms or molecules is responsible for color?

2. In what spectral region do simple organic compounds absorb energy?

3. Why is chlorophyll green?

4. If chlorophyll absorbed light more efficiently, what would the absorption spectrum look like and what color would it be?

Answers:

1. Electronic transitions between different electronic state of atoms or molecules result in absorption of light and is responsible for color.

2. Simple organic compounds absorb in the UV spectral region and appear colorless, because the human eye does not detect in the UV and there is no complementary color.

3. Chlorophyll is green because it absorbs light in the blue and red spectral regions and the reflected light appears green. (See Figure 4).

4. If it absorbed energy throughout the visible, it would appear dark or black.

Chromatics - The Science of Color

Laboratory No. 3-2

Color in Liquids- The Color of Water

Purpose:

To investigate the color of water.

Materials Needed:

Computer with Microsoft PowerPoint for Macintosh version 4.0 or an equivalent program that has a red/green/blue color model.

Discussion:

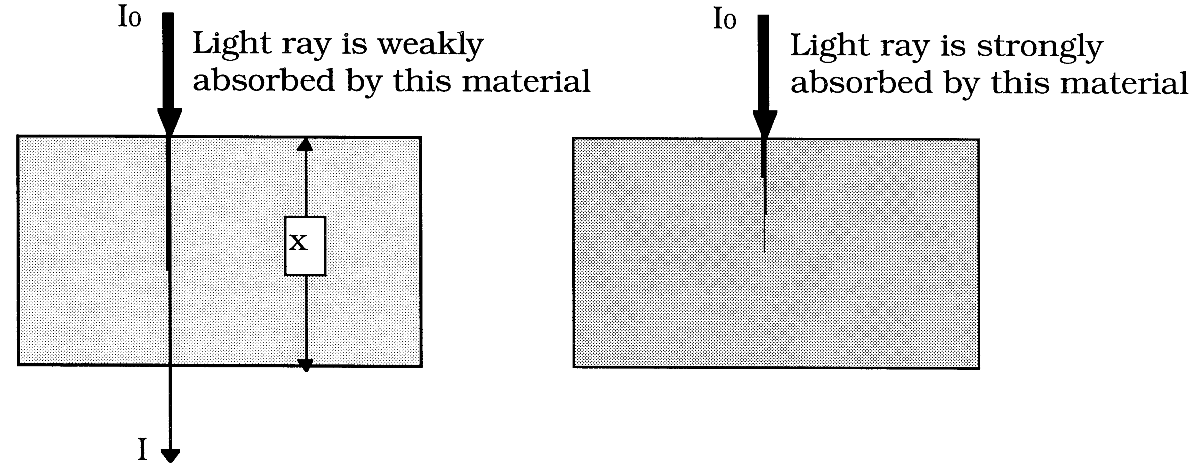
Although water appears to be colorless in the amounts that we typically handle, it is in fact a blue liquid. The blue color is apparent on clear sunny days in the deep ocean, in clear coastal waters and even in swimming pools. Water absorbs strongly in the infrared. In the visible region, it absorbs only weakly in the blue and green regions and begins to absorb more strongly in the red region. In this computer lab experiment, we will see in a semi-quantitative manner how this leads to the blue color of water.

The color of water also depends on how much decomposed plant material, phytoplankton, and particulate matter there is in the water, as well as the intensity of the sun, cloud cover, nature of the water surface, etc. For this experiment, we will ignore these other factors.

First, we need to understand the absorption coefficient of a material. Materials absorb light differently. The absorption of light depends, not only on the incident wavelength of the light, but also on the thickness of the material. This may be described mathematically by the following formula:

$$\frac{I}{I_0} = e^{-ax}$$

In this equation, I_0 is the intensity of the incident light, I is the intensity of the light that has passed through a thickness x of the material, and a is the absorption coefficient of the material. The absorption coefficient a depends on the wavelength of the light. Materials with large absorption coefficients absorb light strongly (are opaque) and those with small absorption coefficients absorb light weakly (are transparent).



Material with weak absorption coefficient a

Material with strong absorption coefficient a

Below is a table showing the absorption coefficient a of water at 3 different wavelengths, corresponding to red, green, and blue light.

Color	Wavelength (nm)	Absorption Coefficient a (m^{-1})
Red	650	0.350
Green	520	0.048
Blue	470	0.016

As an interesting aside, the wavelength dependence of the absorption coefficient of water has apparently determined the wavelength range over which we can see. The absorption coefficient of water is low only in the relatively narrow visible range of the electromagnetic spectrum. In other words, water is quite transparent in the visible region of the spectrum and quite opaque at all other wavelengths. For example, at a wavelength of 60 nm, $a = 10^7$ m^{-1} and at a wavelength of 3000 nm, $a = 10^5$ m^{-1}. This is greater than 10^4 times larger than the absorption coefficient of water in the visible region of the spectrum. Therefore, water is more than 10^4 times more transparent in the visible region of the spectrum than it is at these other wavelengths. Apparently, the eyes of sea animals evolved to take advantage of the transparency of water in the narrow region of the electromagnetic spectrum where water is relatively transparent. They could thus utilize the light that penetrated through the layer of water over them.

It is also interesting to note the significant difference between the human ear and eye. The frequency range over which the ear can hear varies by over a factor of 1000 (from about 20 Hz to about 20,000 Hz). So the wavelength range over which the ear can hear varies by a factor of 1000. In contrast, the visible region over which the eye can see extends from 400 to 700 nm, less than a factor of 2!

Finally, the eye interprets multiple wavelength light as a single color, whereas the ear can distinguish multiple frequencies.

Procedure/Questions:

1. Determine the ratio of the transmitted intensity of light to the incident intensity of light at each of the 3 wavelengths shown above, after light of that wavelength has passed through

   a. 0.1 m of water
   b. 1.0 m of water
   c. 10 m of water.

2. Use the computer program Microsoft PowerPoint 4.0 for Macintosh or equivalent. Select "View" in the menu bar and select "Slides". Then select "Text Color" in the tool bar and select "Other Color." Then select "More Colors." Using the red/green/blue color model, determine the color resulting from the light passing through the amounts of water described in question 1.

3. Suppose that the body of water covered a highly reflective white sandy bottom and you were above the water observing its color. Determine the depth of the water corresponding to light passing through the amounts of water shown in question 1.

4. Explain why water in a small glass appears clear and why water in a deep pool appears blue.

Answers:

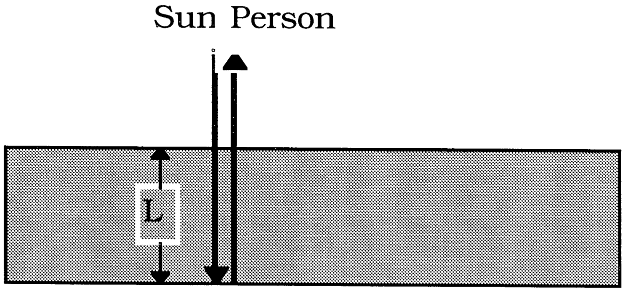
1. a. 0.1 m
red: $I/I_o = \exp\{-(0.350\ \text{m}^{-1})(0.1\ \text{m})\} = 0.97$
green: $I/I_o = \exp\{-(0.048\ \text{m}^{-1})(0.1\ \text{m})\} = 1.00$
blue: $I/I_o = \exp\{-(0.016\ \text{m}^{-1})(0.1\ \text{m})\} = 1.00$

b. 1.0 m
red: $I/I_o = \exp\{-(0.350\ \text{m}^{-1})(1.0\ \text{m})\} = 0.70$
green: $I/I_o = \exp\{-(0.048\ \text{m}^{-1})(1.0\ \text{m})\} = 0.95$
blue: $I/I_o = \exp\{-(0.016\ \text{m}^{-1})(1.0\ \text{m})\} = 0.98$

c. 10 m
red: $I/I_o = \exp\{-(0.350\ \text{m}^{-1})(10\ \text{m})\} = 0.03$
green: $I/I_o = \exp\{-(0.048\ \text{m}^{-1})(10\ \text{m})\} = 0.62$
blue: $I/I_o = \exp\{-(0.016\ \text{m}^{-1})(10\ \text{m})\} = 0.85$

2. a. Using 97% red, 100% green, and 100% blue, the color is white (clear).
b. Using 70% red, 95% green, and 98% blue, the color is a light blue.
c. Using 3% red, 62% green, and 85% blue, the color is a deep blue.

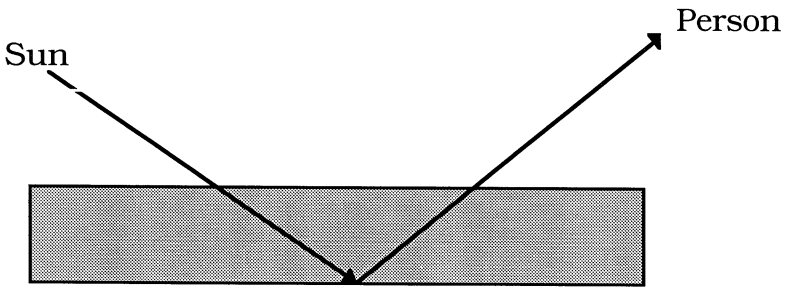
3. The light that is incident from above passes through the water, reflects off of the bottom, and then passes through the water again before it strikes your eye. Therefore the path length of light in the water is twice the depth of the water, so the answers are:



Path length of light in water is 2L.

a. 0.05 m
b. 0.5 m
c. 5 m

Note that this is the maximum depth of the water, since it assumes that the sun and the person are both directly above the water. The path length of light in the water will vary depending on the angle of the person with respect to the sun.



Here, if the path length of light in water is still 2L, then the depth must be less than L.

4. As shown in part a of questions 1 and 2, for a small amount of water, as in a glass, very little of the red component of the light is absorbed. The human eye interprets the resulting color as clear. As shown in part c of questions 1 and 2, for a large amount of water, as in a deep pool, almost all of the red component of the light, some of the green and just a little of the blue component is absorbed. The human eye interprets the resulting color as blue.

Acknowledgment: L. Woolf would like to thank Dr. Sharon Roth Franks of the Scripps Institute of Oceanography for many helpful discussions about this topic, for reviewing and making many suggestions to improve this unit, and for providing a number of useful references.

Chromatics - The Science of Color

Laboratory No. 3-3

Color in Liquids - Acid-Base Indicators

Purpose:

To investigate what acid base indicators are and how they change color.

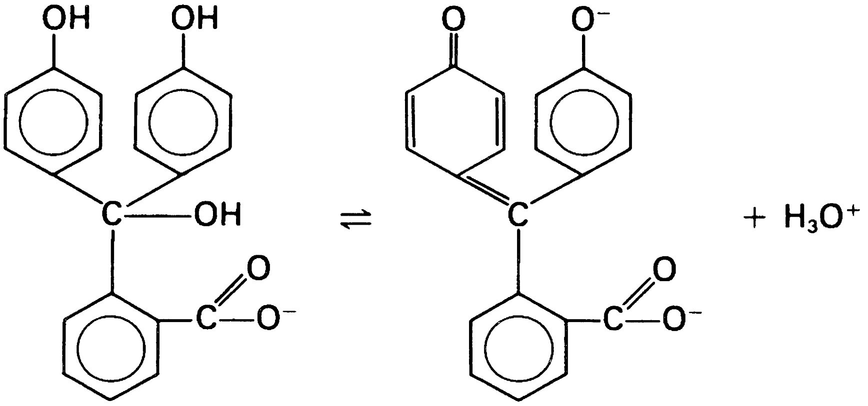
Materials:

1. 0.1 M sodium hydroxide
2. 0.1 M HCl
3. Phenolphthalein indicator
4. Beakers
5. Spectrophotometer (optional)

Discussion:

Acid-base indicators are typically organic compounds that are weak acids. The loss or gain of H^+ ions during a titration is accompanied by structural changes within the acid-base indicator molecule. These structural rearrangements are responsible for the color change. The phenomenon of a change in color with acidity or pH is known as halochromism. The indicator molecule will exhibit continuous structural changes during the titration, but the human eye will not detect these changes until the concentration of the structurally changed molecule is significantly greater than that of the unchanged molecule. That is the pH region where the indicator is useful.

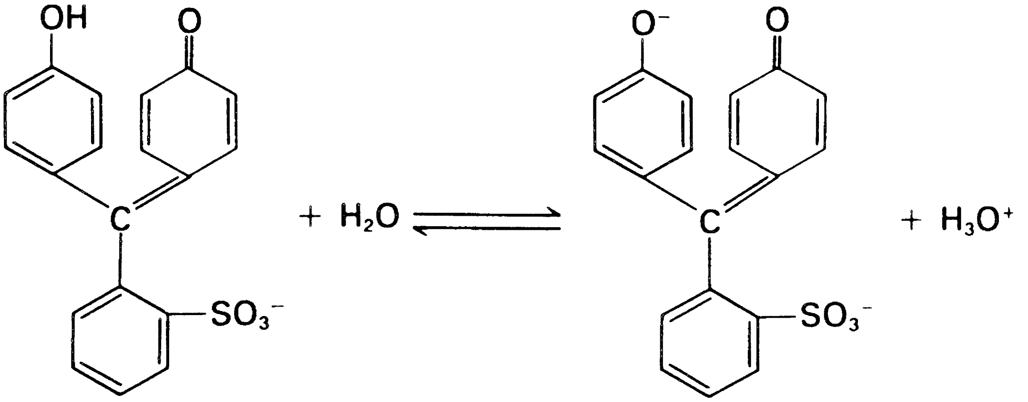
Phenolphthalein is colorless in acidic solutions and red in basic solutions. The exact pH range where the color change occurs is between pH 8.0 and 9.6. The structure of phenolphthalein is:



colorless red

The colorless form contains three substituted benzene rings which do not have an absorption band in the visible. When phenolphthalein is in a basic solution it gives up an H_3O^+ molecule and structurally rearranges to include the formation of a quinoid ring. Now it contains several alternating single and double bonds which absorb in the visible and it appears red.

Another acid base indicator is phenol red, which is yellow in acidic solutions and red in basic solutions. The exact pH range where the color change occurs is between pH 6.4 and 8.0. The structure of phenol red is:



yellow red

The yellow form contains a conjugated system which has an absorption band in the visible and appears yellow. When phenol red is in a basic solution it gives up an H^+ ion and structurally rearranges and it appears red.

Safety:

Do not make contact of strong acids or bases to skin or clothes. If contact occurs immediately rinse with copious amounts of cold water. Do not try to neutralize with another acid or base.

Procedure:

1. Visually determine color of starting solutions.
2. Obtain absorption spectrum of solution with spectrometer.
3. Pour ~20 ml of ~0.1 M HCl in a 100 ml beaker.
4. Place magnetic stir bar in beaker.
5. Pour ~30 ml of ~0.1 M NaOH in a burette.
6. Put several drops of phenolphthalein indicator in beaker.
7. Perform titration.
8. Note volume of NaOH to observe first color change
9. Continue titration. Note volume of NaOH to complete titration.
10. Visually determine color of final solutions.
11. Obtain absorption spectrum of solution with spectrometer.

Questions:

1. What color is phenolphthalein in acidic solutions?

2. What color is phenolphthalein in basic solutions?

3. What molecular structure is responsible for the color in basic solution?

4. What region of the spectrum does the colored solution absorb?

Answers:

1. Phenolphthalein is colorless in acidic solutions.

2. Phenolphthalein is red in basic solutions.

3. A quinoid ring with alternating double and single bonds is responsible for the red in basic solutions.

4. The colored solution absorbs in the blue region of the spectrum and the complementary color is therefore red.

Laboratory No. 3-4

Color in Liquids - Rust and Colors
Charge Transfer Reactions

Purpose:

To investigate charge transfer or redox reactions and how ions in solution can produce color.

Materials:

1. Burette
2. Magnetic stirrer
3. $FeCl_2$, $KMnO_4$, $CuCl_2$, Zn, $AgNO_3$, Cu wire
4. Spectrophotometer (optional)

Discussion:

Oxidation-reduction, or redox reactions, involve the loss and gain of electrons resulting in a change in the oxidation state or oxidation number of the atoms or molecules of the reaction. The oxidation state indicates the net charge of an atom or molecule. Neutral elements are always assigned a 0 oxidation state. For simple ions the oxidation state is the same as the charge of the ion (e.g. Al^{3+} has a oxidation state of +3, Cl^- has an oxidation state of -1)

Most energy producing reactions, including reactions in batteries, fuel cells, metabolism, and fossil fuel burning in power plants and automobiles are redox reactions. In oxidation, a substance loses electrons, and its oxidation number increases. In reduction, a substance gains electrons, and its oxidation number decreases. In any redox reaction the number of electrons lost by a substance must equal the number gained by another. Equations of redox reactions are balanced similar to other chemical reactions with the additional requirement to balance the number of electrons gained and lost.

In the titration of $FeCl_2$ with $KMnO_4$, iron (II) is oxidized

$$5\ Fe^{2+} \leftrightarrow 5\ Fe^{3+} + 5\ e^-$$

and permanganate is reduced

$$MnO_4^- + 5\,e^- + 8\,H^+ \leftrightarrow Mn^{2+} + 4\,H_2O$$

for an overall reaction of

$$5\,Fe^{2+} + MnO_4^- + 8\,H^+ \leftrightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O$$

The K^+ and Cl^- are unchanged in the reaction so are not shown. Due to the color of the reagent and the color of the reduction products no indicator is required for this titration.

In the copper/zinc redox reaction, zinc is oxidized

$$Zn \leftrightarrow Zn^{2+} + 2\,e^-$$

and copper is reduced

$$Cu^{2+} + 2\,e^- \leftrightarrow Cu$$

for and overall reaction of

$$Zn + Cu^{2+} \leftrightarrow Cu + Zn^{2+}$$

The starting solution is blue due to the copper (II) ion. The Zn ion is colorless, so as the concentration of copper ion decreases, the solution loses its color.

In the silver/copper redox reaction, copper is oxidized

$$Cu \leftrightarrow Cu^{2+} + 2\,e^-$$

and silver is reduced

$$2\,Ag^+ + 2\,e^- \leftrightarrow 2\,Ag$$

for an overall reaction of

$$Cu + 2\,Ag^+ \leftrightarrow Cu^{2+} + 2\,Ag$$

The colorless solution turns blue due to the appearance of copper (II) ions.

The metal ions do not exist in aqueous solution in the simple form indicated in the above equations. For example metal ions with a 2+ charge are hydrated in the form

$$M^{2+} + 6\ H_2O \leftrightarrow [M(H_2O)_6]^{2+}$$

Safety:

Normal laboratory safety procedures should be observed.

Procedure:

1. Redox Reaction Titration

1. Visually determine color of starting solutions.
2. Obtain absorption spectrum of solution with spectrometer.
3. Pour ~20 ml of 0.4 M $FeCl_2$ in a 100 ml beaker.
4. Place magnetic stir bar in beaker.
5. Pour ~30 ml of 0.1 M $KMnO_4$ in a burette.
6. Perform titration.
7. Note volume of $KMnO_4$ to turn iron solution purple.
8. Visually determine color of final solutions.
9. Obtain absorption spectrum of solution with spectrometer.

2. Solid/Liquid Redox Reaction

1. Visually or spectrophotometrically determine color of starting solution.
2. Pour ~20 ml of 0.1 M $CuCl_2$ solution in a beaker.
3. Place a ~0.2 g piece of Zn metal in the beaker.
4. Observe "dissolution" of Zn metal.
5. Visually determine color of final solution.
6. Obtain absorption spectrum of solution with spectrometer.

3. Solid/Liquid Redox Reaction

1. Visually or spectrophotometrically determine color of starting solution.
2. Pour ~20 ml of 0.1 M $AgNO_3$ solution in a beaker.
3. Immerse a clean copper wire in the beaker.
4. Observe "whiskers" of silver metal growing from the wire.

5. Visually determine color of final solution.
6. Obtain absorption spectrum of solution with spectrometer.

Questions:

1. What is the oxidation state for each species in the following substances? Ag^+, $2\ Ag^+$, Zn, Zn^{2+}, Cu, Cu^{2+}, H^+, H_2O, Mn^{2+}, and MnO_4^- .

2. What color are copper (II) ions in aqueous solution?

Answers:

1. Ag is +1; 2 Ag is +1; Zn is 0; Zn^{2+} is +2; Cu is 0; Cu^{2+} is +2; H^+ is +1; in H_2O the H is +1 and the O is -2; Mn^{2+} is +2; in MnO_4^- the Mn is +4 and the O is -2.

2. Copper (II) ions are blue in aqueous solutions.

Chromatics - The Science of Color

Laboratory No. 3-5

Color in Liquids - Chemiluminescence

Purpose:

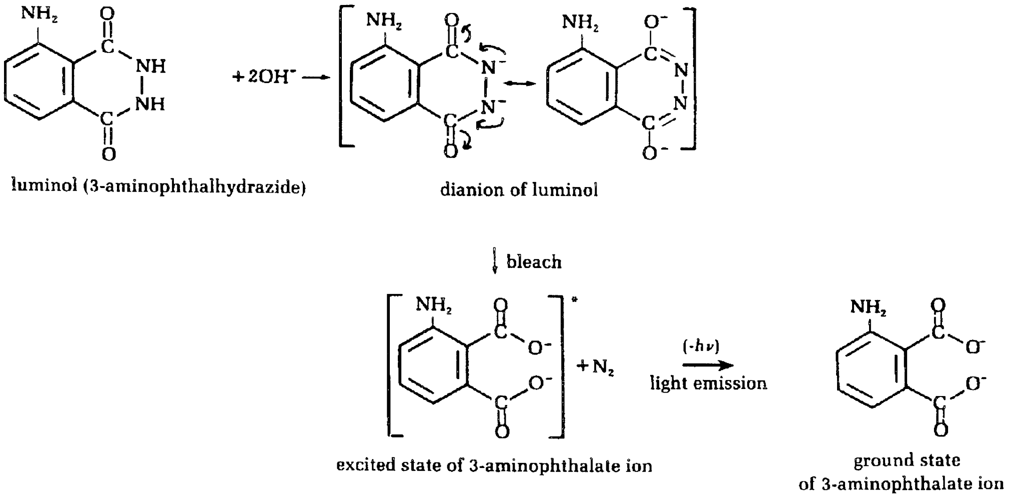
To demonstrate that the reaction of two clear solutions can produce a bright, luminescent color.

Materials:

1. Luminol solution
2. Bleach or H_2O_2
3. Glassware

Discussion:

Liminol is 3-aminophthalhydrazine which is oxidized by the bleach or hydrogen peroxide. During this oxidation the luminol loses nitrogen and gains oxygen according to the reaction:



After the reaction the luminol ion is not in the ground state, but in an excited state. This ion releases the energy of the excited state by emitting a photon to return to the ground state.

Adopted from: L. R. Summerlin and J. L. Ealy, "Chemical Demonstrations", American Chemical Society, Washington, D. C., 1988.

Safety:

1. Wear safety glasses.
2. Wear disposable gloves.

Preparation of Luminol Solution:

Dissolve 0.23 g of luminol in 500 ml of 0.1 M NaOH

Preparation of Bleach Solution:

Dilute 50 ml of commercial laundry bleach (e.g. Clorox, chemically it is sodium hypochlorite, NaOCl) to 500 ml with water.

Preparation of H_2O_2 Solution:

Dilute 25 ml of 3% H_2O_2 (from Drugstore) to 500 ml with water.

Procedure:

1. Place 100 ml of luminol solution in a 400 ml flask or beaker.
2. Darken the room or go to a room that can be darkened.
3. Add 100 ml of bleach solution or H_2O_2 solution to the flask or beaker.
4. Observe the reaction.

Questions:

1. How is the excited state of luminol generated?

2. What does the bleach or H_2O_2 do?

3. By what mechanism is the blue light produced?

4. Approximately what wavelength is the emission?

5. How could you obtain a spectrum of the emitted light?

Answers:

1. The electronically excited state is achieved by chemical oxidation of the dianion of luminol.

2. Bleach or H_2O_2 causes the oxidation of the luminol dianion by removing nitrogen and adding oxygen to the molecule. No heat is evolved during this oxidation step; rather the energy transforms the molecule to the excited state.

3. The excited state of luminol relaxes to the ground state by emitting a photon of blue light.

4. The broad band emission centers around 400 nm (any answer between 350 and 450 nm should be considered correct).

5. Place a cuvette or test tube of activated luminol solution in an emission spectrophotometer and quickly scan the wavelengths.

4. Color in Solids

There are many different types of solids, which can be broadly classified as covalently bonded solids, ionic solids, and metals. Covalent and ionic solids can be crystalline in structure and have different causes of color than found in metals. The color in most solids is due to chemical causes, that is the absorption of a photon by an electron in an orbital that is promoted to an excited state. The energy of the photon corresponds to the energy of the electronic transition. The photon has a particular color associated with it and the complement of that color is the color of the solid. There are many different causes for the absorption of photons by solids which depend on the exact electronic states the atoms or groups of atoms involved in the transition.

In transparent crystalline materials, the electrons are generally more strongly bound so they do not interact with visible light. This is observed in the fact that materials such as glasses, or minerals such as quartz , and even common table salt, are electrical insulators, and are generally colorless. Yes salt is colorless, not white. Look at it under a microscope or magnifying glass. The white appearance comes from multiple scattering from the many small crystals, so all wavelengths are scattered uniformly back to the eye. A similar type of scattering effect, called Mie scattering, is responsible for the opaque white color of clouds, which consists of colorless water droplets. Similarly white paint derives its whiteness and opacity from multiple scattering from many transparent microscopic crystals of titanium dioxide that are added to paint as an opacifier. However, we all know that many minerals are vividly colored which gives them great value as gemstones. This arises from the presence of minute quantities of crystalline defects that produce localized loosely bound electrons that can interact with visible light of very specific wavelengths. Well known examples are ruby and sapphire which are both crystalline aluminum oxide, differing only in the presence of minute quantities of metallic impurities that produce defects known as color centers. Aluminum oxide in its pure state is colorless and transparent. It forms on all bare aluminum when it is exposed to air and forms a transparent protective layer that inhibits further corrosion. It is also widely used as a high quality electrical insulator, and is one of the hardest crystals known. The addition of minute quantities of chromium to aluminum oxide produces the vivid red color characteristic of ruby, while small amounts of titanium produce the blue of sapphire.

In metals the bonding electrons are delocalized in a band that allows electrons to move freely. This accounts for the good electrical and thermal conductivities of metals. Due to this band of free electrons there are no distinct orbitals and all photons are strongly absorbed. This strong absorption is the cause for a quick re-emission which results in the strong reflection of smooth metal surfaces. If the surface is roughened, it will look dull or even black due to multiple scattering or loss of reflectivity. Some metals, like copper or gold have color associated with them due to some variation in the absorption coefficient with the photon energy. Because copper and gold do not absorb the blue region of the spectrum as well, they also do not re-emit or reflect it as well, leading to the reddish and yellowish colors, respectively.

Chromatics - The Science of Color

Laboratory No. 4-1

Color in Solids - Interference Colors

Purpose:

To demonstrate how diffraction and interference of light waves can produce colors.

Materials:

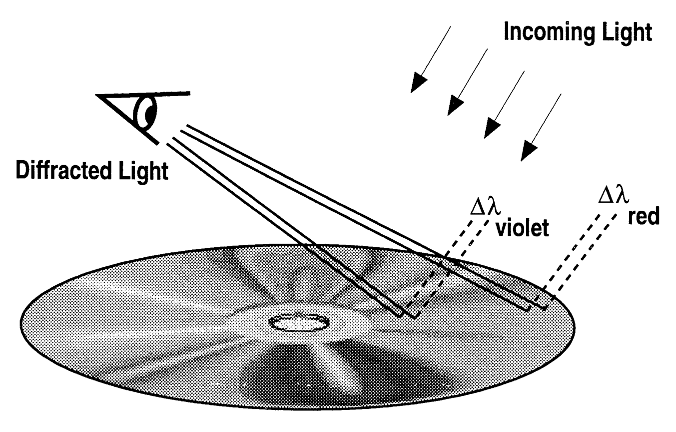
1. Audio CD
2. Glass slides (2 per student or team) or soap solution and wand
3. Peacock feather
4. Mercury light source
5. Incandescent light source.

Discussion:

One of the most interesting property of waves is called *interference.* Interference occurs when two waves overlap and combine with each other. The new wave that results is the sum of the effects of each wave. Interference can be either *constructive* or *destructive.* By getting one light wave to travel one wavelength farther than the other, the peaks and troughs add constructively to produce a bright image. However, if one of the waves travels a half wavelength farther than the other, the peaks and troughs are out of phase and the light rays combine destructively so no light will be seen.

How do we manipulate light waves so their peaks and troughs align? Interference patterns with light are usually produced by splitting a light beam into two or more parts and recombining them. To do this we use another wave phenomenon known as *diffraction.* Diffraction is the bending of waves around sharp corners or edges which causes the waves to spread. The diffracted light waves interfere with each other and produce an interference pattern. In 1801 Thomas Young did an experiment with pinholes to diffract sunlight, producing an interference pattern on a screen. This experiment provided the first convincing evidence of the wave nature of light!

Young's experiment is done today with slits instead of pinholes. However, the production of an interference pattern is not limited to slits and pinholes. In order for diffraction to be noticeable, the object causing the spreading must be about the same size as the wave. For visible light, this is only hundreds of nanometers! When light is incident upon a surface with parallel grooves or other regular structures which are spaced several hundred nanometers apart, such as the grooves in an audio CD or diffraction grating, light is diffracted and an interference pattern results. The color of the reflected light will depend upon the viewing angle. Figure 1 shows the wavelength you see is equal to the path difference, $d \sin\Theta$, of the interfering light beams when viewed at an angle Θ to the surface. Such colors from interference are called *iridescence.* Similar phenomena are observed in nature.



Why are there colors in a compact disk?

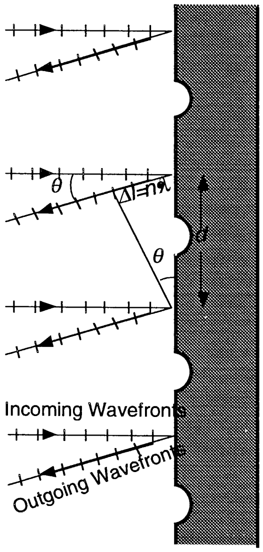


Figure 1. Light reflected from the grooves in a CD interferes with itself and produces a color which is determined by the viewing angle.

The shells and wings of some beetles and butterflies have parallel grooves that produce iridescence. Iridescent butterflies have scales that act as reflective gratings. (There's a great exhibit of morpho butterflies in the basement of the Museum of Natural History in Balboa Park.) The bright "eyes" in a peacock's feather and the colors on the throat of hummingbirds are also due to iridescence. The surface of the feather contains hundreds of fine rods which cause incident light to interfere with itself and produce the intense colors that we see.

Iridescence can also come from constructive reflections of thin films such as soap bubbles or oil on water and is an indication of the film's thickness. Light rays are reflected from both the inner and outer surfaces of the film and therefore travel different distances. If the difference in distance is a multiple of a color's wavelength, that color is produced. Dark spots on the film's surface are areas where the wave fronts cancel or destructively interfere, producing no color.

These objects, natural or man-made, disperse white light into colors. Whereas a prism separates the colors of light by refraction, diffraction causes separation of color by interference. If the incident light is monochromatic (composed of a single wavelength), the interference pattern will be composed of a series of well-determined lines. The wavelength of the illuminating light can be determined with a simple optical bench by measuring the spacing of these lines.

Procedure:

1. Take a normal audio CD to an incandescent light and examine the interference pattern that results from reflected light. What colors do you see and in what order? Compare what you see to a rainbow.

2. Examine the CD in front of a mercury light source. hat colors do you see? hat does this tell you about the wavelengths of light emitted by excited mercury gas? Do you see color at more than one viewing angle? Why?

3. Dip a wand into a soap solution (dish washing liquid), and then hold it sideways and look at the reflected light from the soap film that covers its mouth. (Looking with the wand against a dark background may help see the

colors.) What types of patterns do the colors make? Is there color everywhere? If the film is thicker at the bottom than at the top, can the same colors appear in both areas? Why? What do you think is happening in the black areas? Blow a bubble through the wand. Are the same colors that you saw in the film visible on the bubble's surface?

4. Press two glass slides together and view them at an angle. Describe what you see. Try pressing a thin hair in between the slides near one end to make a wedge. Now what do you see?

5. Are the brilliant feathers of a peacock really blue and green? Look at a peacock feather at different angles and notice how the color changes. Are the colors due to pigmentation or interference?

Answers:

1. The colors observed are the colors of the rainbow and they appear in the same order as colors in a rainbow (Roy G. Biv).
2. Blues/purples are the colors observed in mercury light since these are the only wavelengths of light produced by a mercury lamp. Colors are viewed at more than one viewing angle as we move through different "orders" of constructive interference (n = 1, 2, 3 etc.).
3. The colors on the surface of a thin film of soap and a soap bubble are all due to thin film interference and are the same colors. The colors are produced when a particular wavelength satisfies the criteria for constructive interference off the front and back surface of the soap film. Black areas are regions of destructive interference - no colors are produced. The soap bubble's thickness determines which colors will be seen as different wavelengths of light will fit into different areas of thickness. Two thicknesses of film may produce the same color if both are a multiple of a quarter wavelength of that color. When a film becomes too thin, no visible light waves will meet the interference criterion and therefore no color will be seen (black).
4. An interference pattern may be set up by trapping a volume of air between two glass slides. The pattern produced is a series of swirls, much like in a soap bubble but not as dynamic. Adding a single hair between the two slides increases the gap and creates a thicker film. The patterns should be the same in both cases.

5. The blue and green colors of a peacock's feather are due to interference. The feather consists of a regular, closely spaced structure that traps air and causes the colors we see. Move the feather at various angles and notice the colors get duller. Add a drop of acetone or alcohol to the feather and notice the color changes! This is due to the solvent having a different refraction index so that the light waves are bent a different amount as they interact with the feather's structures. A different color light now reaches our eyes.

Chromatics - The Science of Color

Laboratory No. 4-2

Color in Solids - Black Lights and Fluorescence

Purpose:

To investigate how UV light may be detected although we cannot see it directly.

Materials:

1. UV light source (black light)
2. Plastic goggles
3. Fluorescent crayons or paint, minerals, shells, laundry detergent, or other material the student may want to bring from home.
4. Suntan lotion

Discussion:

Atoms can become excited by *absorbing* high energy light and also de-excited by *emitting* light of lower energy. Ultraviolet (UV) is energetic light that is invisible to our eyes. It has a wavelength range of 5 to 400 nm, placing it between visible light and x-rays in the electromagnetic spectrum. It has a shorter wavelength and therefore more energy than visible light. Many atoms can absorb invisible light such as UV and then spontaneously emit less energetic (longer wavelength) visible light. This way of giving off light is called fluorescence.

A familiar example of fluorescence is the common fluorescent lamp you might be sitting under right now. In a fluorescent lamp, oscillating electrons excite atoms of mercury gas, which then give off photons of intense and invisible ultraviolet light. The inside surface of the lamp is covered with a powdery fluorescent material called a phosphor, and this material first absorbs the UV photons and then emits photons of visible light. The excited atoms in the phosphor take several steps, or transitions, to return to their original energy or ground state. Each step results in the emission of less energetic photons that have frequencies in the range of visible light which combine to produce white light. The atoms of each element have a unique set of wavelengths for the absorption and emission of light, depending on the different possible energy states the atoms possess. Therefore, phosphors of different elements can be used to produce different colors of light.

Fluorescence is responsible for the appearance of objects under a "black light" which is a source of ultraviolet radiation. Normal sunlight is most intense in the yellow region of the visible spectrum; these photons cannot produce emissions in frequencies (energies) greater than yellow. Objects seen in UV light may therefore show a stronger blue or violet response than when viewed in sunlight.

Because the fluorescence frequencies are different for different substances, fluorescence is a powerful tool for identification of rocks, minerals, and other compounds. It is also used for assaying - determining how much of a substance is present - in plants and animals.

Procedure:

Follow the instructions for eye protection that come with your UV light source!

1. Assemble a variety of objects, including rocks and minerals, starched fabric, and other everyday objects. Describe each object as viewed in sunlight or fluorescent lighting. Turn on the UV light source and view each of the objects again. (The effects are best observed in a dark environment. If the classroom cannot be darkened, place the object in a box which has a hole cut into the top of it to allow the objects to be illuminated and another hole in the side so that you may observe the effects.) Record your observations.

2. Place suntan lotion on a portion of an object that fluoresced in the first step. Turn on the UV light source and record your observations.

Questions:

1. Why do some laundry detergents make your clothes "whiter than white"?

2. UV light is invisible to the human eye. How would you detect the presence of UV light?

3. Why can different fluorescent materials produce different colors of visible light?

4. Can infrared light produce visible light via fluorescence? Why or why not?

5. Why does the suntan lotion alter the fluorescence of objects?

Answers:

1. Laundry detergents contain a fluorescent material that responds to the UV component of ordinary sunlight. Clothes viewed in sunlight weakly fluoresce, causing the sensation of a brighter color.

2. Use a material know to fluoresce in UV light. The invisible UV light will be converted to a visible wavelength which we can then detect with our eyes.

3. The color of light produced during fluorescence depends upon the electronic structure of the elements of the material. Different materials may absorb UV at slightly different wavelengths, resulting in different fluorescent colors.

4. No, infrared light cannot produce visible light via fluorescence as the emitted light is always lower energy, higher wavelength light. IR light is at the upper wavelength limit of what we can detect with our eyes, so any "light" produced above IR will not be visible to us.

5. Many suntan lotions contain UV-absorbing chemicals. When the UV is absorbed, it can no longer cause fluorescence.

5. Dynamic Colors

There are a number of compounds that change color in response to an external change. For example, certain chemicals will change color in response to a change in temperature; this effect is called thermochromism. As the temperature changes the lattice structure of the material is modified by changing the relative positions of atomic neighbors. This affects the way the atoms interact with each other and alters the material's absorption characteristics. So called mood rings, stress indicators, and fever monitors contain organic dyes, such as anil, which undergo reversible structural changes with temperature that result in a change of color. Some inorganic compounds undergo irreversible structural changes and are used for temperature indicating paints and dyes. Beside thermochromism, there is photochromism, which is a color change due to the interaction with light; piezochromism, due to change of pressure; halochromism, due to change in acidity or pH; and electrochromism, due to change in applied applied potential.

The first experiment in this section explores the color differences of a salt when it is in a hydrated and dehydrated state. Here, the structure of the compound is changed on the atomic level and the result is macroscopic change which is percieved as a change of color.

Electrical current can be used to dynamically alter the color of a material. Ions are injected or removed from the crystalline lattice, thus altering the absorption spectrum (color) of the material. Or thin films may be repeatedly plated and stripped on a transparent medium, resulting in light modulation. This type of color control is being used in variable-tint automobile windows and is the subject of our investigation in the second experiment of this section.

Many animals have the ability to change color. The color change we perceive in a chameleon for example is in response to light intensity. Many squids, octopuses, and other fish also are quick change artists. These animals are responding to changes in temperature or mood which affects their color-containing cells or chromatophores via a hormone-induced reaction. Various shades and patterns of colors are produced using the mechanisms of color mixing and/or interference, sometimes almost instantaneously as in squids and octopuses. (For a better description of the color changes observed in squids and octopuses, see the Critter Watch article "Colour Me Moody" by Richard Martin at http://www.uvsports.ycg.com/magazine/1995/november_december/marinlif.htm.) Many of these animals have melanin in pigment-containing cells that aids them in their ability to change color. Melanin is the same substance which colors human skin brown and causes the tanning effect due to exposure to sunlight. Also, apples and bananas contain melanin, which upon exposure to air oxidizes and turns brown.

Chromatics - The Science of Color

Laboratory No. 5-1

Dynamic Colors - Thermochromics

Purpose:

To investigate how some compounds change color with temperature.

Materials:

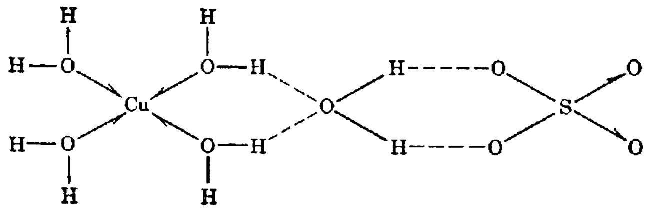
1. Copper Sulfate
2. Hot plate or Bunsen burner
3. Spectrophotometer (optional)

Discussion:

In most solids, atoms and ions are located in a crystalline lattice structure. Each atom or ion is surrounded by a fixed number of nearest neighbors. Depending on the type of lattice this could be 4, 6, or 8, known as the coordination number. The potentials from the various neighbors sum to a particular value and result in a field surrounding the central ion. Historically, these considerations were first applied to crystalline materials, hence the potential was called a crystal field. Later this theory was expanded to include non-crystalline materials and to describe how nearest neighbors influence any ion or atom. The term ligand field theory is used for the more general case.

Transition metal ions in a lattice structure or in aqueous solution frequently exhibit bright colors. In aqueous solution the ions are surrounded by water molecules in a ordered structure due to the polar nature of the water molecule. The transition metals which display the most color, generally have unpaired electrons in d or f orbitals. The primary absorption band is in the red and infrared. Recall that an absorption in one part of the spectrum gives the material its complementary color. Therefore, an absorption band in the red results in a blue material. For this reason, solutions of divalent copper salts have a characteristic blue color.

Copper sulfate is normally found in the 5 hydrate form, $CuSO_4 \cdot 5H_2O$. Four water molecules are bonded to the copper ion as coordinated water. The fifth molecule is hydrogen bonded between the coordinated water molecules and the sulfate ion. A crude representation is as follows:



This arrangement creates a ligand field as discussed above. The copper ion is completely surrounded by water molecules in this structure. Upon heating, this salt dehydrates in steps yielding the $CuSO_4 \cdot 3H_2O$, and then the $CuSO_4 \cdot H_2O$. Between 200 and 300 °C, it loses the last water molecule. In the absence of water molecules the ligand field disappears and the compound loses its color. This is one mechanism where compounds can change color with temperature.

Minerals, gems, ores, and pigments are generally inorganic compounds containing transition metal ion impurities with unpaired electrons in d or f orbitals. The ligand field in these materials can be affected by a number of external factors, such as pressure and temperature. Compressing a crystal can shorten the bond lengths of the atoms and increase the ligand field. This can result in a color change and is called *piezochromism.* Upon heating a crystal, the atoms gain vibrational energy and the lattice spacing increases, reducing the ligand field. This can result in a color change and is called *thermochromism.*

Safety:

1. Wear safety glasses when heating substances on a hot plate or open flame.

Procedure:

1. Place ~1-2 of Copper sulfate in a crucible.
2. Observe color of the copper sulfate
3. Slowly heat to ~300 °C on a hot plate or Bunsen burner.
4. Observe color changes with temperature.

5. Remove crucible from heat and let cool to room temperature.
6. Add a few drops of water to dehydrated copper sulfate and observe color change.
7. Dissolve 1-2 g of copper sulfate in ~10 ml of water.
8. Obtain absorption spectrum of solution with spectrometer.

Questions:

1. What form is copper sulfate normally found in?

2. What is the approximate wavelength of the absorption?

3. Why does dehydrated copper sulfate lose its color?

4. How could you build a chemical moisture indicator?

Answers:

1. Copper sulfate is normally found in the hydrated form. It normally contains five water molecules.

2. The primary absorption is in the red and infrared region of the spectrum, which is in the wavelength range of 650 to 750 nm.

3. The hydrogen bonded water molecules create a ligand field that is responsible for the electronic transitions and the color. When the copper sulfate loses the water molecules, the ligand field is destroyed and the color is lost.

4. You could place dehydrated copper sulfate in a clear plastic bag or container with small holes in it. As water is absorbed, the copper sulfate will turn blue, indicating the presence of moisture.

Chromatics - The Science of Color

Laboratory No. 5-2

Dynamic Colors - Electrochromics

Purpose:

To investigate the electrochromic color change in thin film Prussian Blue.

Materials:

1. 2 AA cell battery holders and batteries
2. 2 momentary switches (1 red, 1 black)
3. Black and red colored wire (24-28 gauge)
4. Alligator clips
5. ITO coated glass or plastic strips (furnished)
6. $FeCl_3 \cdot 6H_2O$
7. $K_3Fe(CN)_6$
8. HCl
9. KCl
10. Pipetter (if stock solutions of items 6 and 7 are desired for dilution)
11. Ag wire
12. Cu tape or Ag paint
13. Solder and soldering iron
14. Digital multimeter.

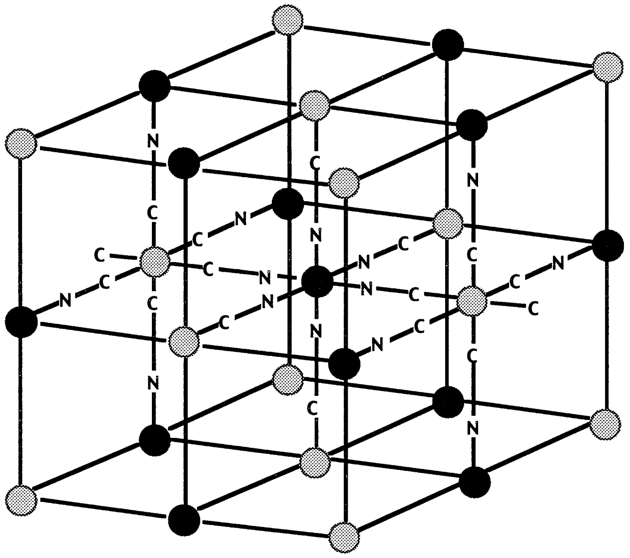
Discussion:

Electrochromic (EC) materials change color reversibly with applied electrical current. Many materials are known that exhibit *electrochromism* (a solid state effect) or e*lectrochemichromism* (an electrochemical effect). Both effects are generally referred to as electrochromism and are not distinguished hereafter. EC materials can be broadly classified as follows:

Ion insertion materials, in which thin electrochromic films attached to transparent conductive substrates are switched by the simultaneous insertion (or ejection) of ions and electrons into the material. Examples include WO_3, Prussian Blue, and conducting polymers. *Reversible electro-deposition materials*, where thin films are repeatedly plated and stripped from a transparent conductive substrate, resulting in light modulation. Examples include organic compounds like viologens and quinones, and metals such as silver and copper.

Solutions, such as the dyes from section 3.2, that can be switched electrochemically to drive the color change reaction.

In this laboratory the student will grow a thin film of Prussian Blue (PB) onto a transparent conducting substrate and electrochemically effect color switching in the thin film. PB has found wide use as a paint pigment and its structure is presented below



PB has an open cubic structure comprised of iron (Fe) atoms linked by cyanide (CN) bridging ligands. For clarity, interstitial ions and molecules are not shown. Careful inspection of the structure reveals that there are two distinct types of octahedrally coordinated Fe atoms in the lattice. One type of Fe is surrounded by carbon (C) atoms while the other is surrounded by nitrogen (N) atoms. The coordination of the Fe atoms corresponds to a particular electronic energy structure according to the ligand field theory mentioned in section 3.3. In particular, the electronic energy structure of the Fe atoms surrounded by N atoms is responsible for the intense blue color of PB. The main color switching reaction in PB is believed to proceed as follows:

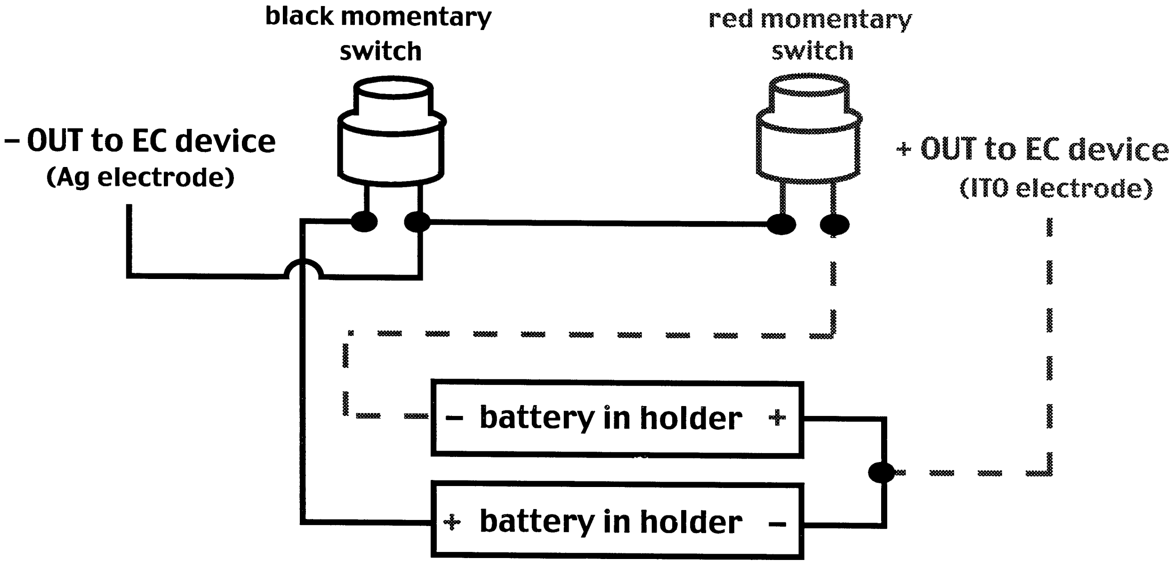
$$Fe_4^{3+}[Fe^{II}(CN)_6]_3 + ne^- + nK^+ = K_nFe_4^{2+}[Fe^{II}(CN)_6]_3$$

where $Fe_4^{3+}[Fe^{II}(CN)_6]_3$, Fe^{n+}, Fe^{II}, K^+, and $K_nFe_4^{2+}[Fe^{II}(CN)_6]_3$ are PB, high spin iron, low spin iron, potassium ion and Prussian White, respectively. Cations and electrons are intercalated into the lattice and reduce the high spin Fe atoms that are octahedrally coordinated to the N atoms. The cations occupy interstitial sites in the PB lattice. The end result is that the electronic structure of the material changes and results in a color change. This reaction is reversible and the system enjoys a lifetime of more than one million switching cycles under controlled conditions.

Safety: Acids should be handled in a fume hood. Safety glasses and gloves should be worn. Be careful when soldering, the hot iron and molten solder can cause burns.

Procedure:

1. Prepare the following electrochromic device switcher. This configuration allows the electrode potential to be reversed by pushing one switch or the other. Note: the dashed lines are red wires.



2. Prepare a fresh 100ml solution containing equimolar amounts of $FeCl_3 \cdot 6H_2O$ and $K_3Fe(CN)_6$. The concentration of each should be 5mM.

3. Prepare a stock solution of 1 M KCl and adjust the pH of the solution with dilute HCl to a value between 3 and 4.

4. Obtain a 1.5" strip of 1mm diameter Ag wire. The Ag wire will be used as a sacrificial anode to drive the Prussian Blue (PB) film formation reaction. The same wire will later be used as the counterelectrode in the electrochemical cell.

5. Make contact to the ITO coated glass (or plastic) substrate using Cu tape or Ag paint and a wire with alligator clips on each end.

6. Place the substrate in the solution. Do not allow the solution to wick up and touch the Cu or Ag contact. Place the Ag wire into the solution facing the conducting side of the substrate. Only put the top 0.25" of the wire into the solution. The film is now growing.

7. Let the film grow for 30 minutes. Remove from the growth solution and rinse with water. Observe the color of the as-grown PB film. After the first growth run, the experimenter can vary the growth time using a fresh substrate and observe the results.
8. Place the substrate/PB film into a 100 ml beaker containing the pH adjusted KCl solution. Clean the Ag wire by rinsing with water, dry it with a clean cloth and place it in the solution facing the PB. Use wires with alligator clips on each end to connect to the PB and Ag electrodes.

9. Connect the red + OUT wire to the red wire on the voltmeter, and the black - OUT wire to the black wire on the voltmeter. Using the voltmeter, determine the voltage obtained when first the red switch is depressed and again when the black switch is depressed. Write this down in your notes. Connect the Ag electrode to the black - OUT wire and the PB (ITO) electrode to the red + OUT wire on the electrochromic device switcher.

10. **Very quickly** push the correct switch to apply a negative bias to the PB electrode and then release it. The circuit should only be complete for a fraction of a second. Observe what has happened to the PB electrode. What color does the film appear now?.

11. Now **very quickly** push the other switch to apply a positive bias to the PB electrode and then off. What color is the film now?

If the experiment has been performed correctly the PB film will have reversibly switched without any deleterious side reactions. The student can now continue to switch the PB film on and off and explore the coloration of the material.

Questions:

1. What is the oxidation state of iron in $FeCl_3 \cdot 6H_2O$? How about in $K_3Fe(CN)_6$?

2. Balance the equation: $Fe_4^{3+}[Fe^{II}(CN)_6]_3 + ne^- + nK^+ = K_nFe_4^{2+}[Fe^{II}(CN)_6]_3$.

3. Describe what happens in the electroless deposition of Prussian Blue in terms of what chemical species get oxidized or reduced.

4. What color is the as-grown film? What color is it after it gets switched in step 10 of the experiment?

5. Is the reaction in Question 2 an oxidation or a reduction reaction as written (i.e. from left to right)? What species, if any, get oxidized or reduced?

Answers:

Teachers Note: It is usually helpful to prepare stock solutions of chemicals prior to performing experiments. The stock solutions are then diluted later when the experiment is performed. For example, one might prepare 1M solutions of $FeCl_3 \bullet 6H_2O$ and $K_3Fe(CN)_6$, which are diluted and mixed when the experiment is performed. To do this one needs a pipetter of some kind. In order to prepare stock solutions of chemicals the following formula weights will be useful:

$FeCl_3 \bullet 6H_2O$	fw 270.30
$K_3Fe(CN)_6$	fw 329.26
KCl	fw 74.56

1. The oxidation state of iron is 3+ in both $FeCl_3 \bullet 6H_2O$ (iron chloride hexahydrate) and $K_3Fe(CN)_6$ (potassium ferricyanide).

2. $Fe_4^{3+}[Fe^{II}(CN)_6]_3 + 4e^- + 4K^+ = K_4Fe_4^{2+}[Fe^{II}(CN)_6]_3$

3. From the answer to question 1 we know that the starting materials both contain Fe in the 3+ oxidation state. Question 2 shows that PB contains Fe in both 2+ and 3+ oxidation states. Further, by inspection of the chemical formula it appears that the Fe from iron chloride remains in the 3+ oxidation state and the Fe from potassium ferricyanide gets reduced to 2+. Hence, during the electroless growth of PB from solution the Ag wire gets *oxidized* to Ag^+ driving the *reductive* formation of PB.

4. The as-grown film is blue (hence the name Prussian Blue). The film turns clear after it gets reduced in step 10 and becomes Prussian White (PW). Referring to the equation from question 2, as the reaction proceeds from left to right the blue PB film is switched into the colorless PW film.

5. To determine whether the reaction is an oxidation or reduction we must determine what is happening with the electrons. Reduction can be thought of as "adding electrons" to something. In this case, electrons are added to the high spin Fe^{3+} and this species is reduced to Fe^{2+}. This changes the electronic structure of the material and hence changes its color. Equation 2 is a reduction reaction as written, PB is getting reduced to PW.

Bonus Question: What happens if PB becomes oxidized?

Answer to Bonus Question: This can be used by the instructor as a hint to answer some of the other questions. The answer requires the student to apply a positive bias stepwise to the PB film. A voltage divider would be useful here as different compounds appear at different potentials. If done carefully, one can observe first a green color (Berlin Green) and then a yellow color (Prussian Yellow). These compounds are not very stable, however, and may peel from the ITO coated glass. For this reason, only the blue (PB) and clear (PW) compounds are important in practical devices.

References

Web Sites

Best Sites

http://www.education.siggraph.org/hypgraph/color/color0.htm
Color Models

http://www.wasatchinc.com:80/digigrafix.html
Color Management

http://www.wasatchinc.com/digigrafix.gamut.html
Color Gamut and Gamut Mapping

http://www.tek.com/Color_Printers/reference/colrbas.html
Tektronix Computer Color

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http://cc.oulu.fi/~kempmp/pyro.html
Pyrotechnics

http://cc.oulu.fi/~kempmp/colours.html
The Physics of Coloured Fireworks

http://www.isc.tamu.edu/~astro/color.html
Color Science

http://www.inforamp.net/~poynton/notes/links/color-links.html
Poynton's Color links

http://www.inforamp.net/~poynton/
Charles A. Poynton

http://www.wasatchinc.com:80/links.htm
Some Links

http://www.pantone.com/
Pantone Home Page

http://www.tek.com/Color_Printers/cool_stuff/templt.html
Print from These Templates

http://lainet3.lainet.com/~ausbourn/
Optical Illusions

http://www1.mhv.net/~LE/welcome.html
Stage Lighting - Lighting & Electronics' Home Page

http://world.std.com/~wij/color/index.html
Through the 6x6x6 Color Cube: An Interactive Voyage

http://www.scvnet.com/~weber/index.html
Web Color Charts plus Links

http://info.mcc.ac.uk/CGU/ITTI/Col/colour_announce.html
Colour in Computer Graphics

http://www.graphics.cornell.edu/KOC95/color/color.html
Color

http://www.education.siggraph.org/hypgraph/hypgraph.htm
HyperGraph

http://cvision.ucsd.edu/index.htm
CVRL Color & Vision database

http://www.artstuff.com/class/accolor2.htm
Colors, 2 of 4

http://www.mcn.org/MenComNet/Business/Retail/Lib/ColorTheory.html
COLOR THEORY and Mixing Stains or Dyes for the Woodworker & Furniture Finisher

http://www.pubserv.washington.edu/Color.Theory/Color.Theory.html
Color Theory

http://www.contrib.andrew.cmu.edu:8001/usr/dw4e/color/links.html
Color Theory -- Other Color Pages

http://www.contrib.andrew.cmu.edu:8001/usr/dw4e/color/wheel.html
Color Theory -- Color Wheel

Books

Blue and Yellow Don't Make Green, Michael Wilcox, North Light Books, F & W Publications, Inc., 1994.

Color Analyzers (Grades 5-9), one of the Great Explorations in Math and Science (GEMS) units, available from the Lawrence Hall of Science, (510)-642-7771.

Colour: Art and Science, edited by Trevor Lamb and Janine Bourriau, Cambridge University Press, 1995.

Color Theory and Its Application in Art and Design, G. A. Agoston, Springer Verlag, 1987.

Evolution in Color, Frans Gerritsen, Schiffer Publishing Ltd., 1988.

Color Atlas: A Practical Guide for Color Mixing, Harald Kueppers, Barron's Educational Series, Inc., 1982.

Articles

"Who Invented the Color Wheel," C. Parkhurst and R. L. Feller, Color Research and Applications, Volume 7, Number 3, Fall 1982, pp. 217-230.

"Evolution of the Color Diagram," F. Gerritsen, Color Research and Applications, Volume 4, Number 1, Spring 1979, pp. 33-38.

"Colour Teaching - A New Color Circle" by F. Gerritsen, pp. 494-498 in Colour 73, Survey Lectures and Abstracts of the Papers Presented at the Second Congress of the International Colour Association, John Wiley and Sons, 1973.

Materials List

1. The handheld microscopes, which contain both a 30 x light microscope and an 8 x magnifier, are available from Radio Shack for about $ 8. They are called the Radio Shack 30 x Illuminated Microscope, catalog number 63-851. It requires 2 AA batteries.
Needed for Laboratories 1-2, 1-3, and 1-4.

2. Transparent films of red, green, blue, cyan, magenta and yellow can be obtained from the General Atomics Sciences Education Foundation (http://www.sci-ed-ga.org/modules/materialscience/color/materials.html).
Needed for Laboratory 1-3.

3. Rainbows can be projected onto the classroom wall or on a screen using an overhead projector and a diffraction grating.

Sheets of holographic diffraction grating can be purchased from Learning Technologies, Inc. 1-800-537-8703.

Sheets can also be ordered from Edmund Scientific
$10.00 each for a 12 inch x 6 inch sheet Part Number C52,990

Diffraction gratings mounted in 2 inch x 2 inch slides can also be ordered from Edmund Scientific in

Package of 15	Part Number C52,991	$15.95
Package of 25	Part Number C52,992	$24.50
Package of 80	Part Number C52,993	$61.00.

Needed for Laboratory 1-1.

General Atomics Sciences Education Foundation Web Site

Visit http://www.sci-ed-ga.org to obtain:

- Additional information about the General Atomics Sciences Education Foundation
- Additional information about this and other educational modules developed jointly by General Atomics scientists and San Diego area teachers
- Answers to questions that you can post to the Chromatics forum. The forum allow you to interact with other teachers using this modules as well as with the scientists and teachers who developed the Chromatics module.