Experiments on subtractive color mixing with a spectrophotometer

P. U. P. A Gilbert and Willy Haeberli

Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

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We describe experiments on color mixing suitable for undergraduate nonscience majors. A commercial spectrophotometer is used to study the spectra of light sources, combinations of color filters, and mixtures of acrylic paints. Special emphasis is placed on teaching the fundamentals of subtractive color mixing and the complex processes that occur in mixing pigments. © 2007 American Association of Physics Teachers.

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I. INTRODUCTION

The experiments described in this paper were developed as part of a laboratory for a “Physics in the Arts” course for undergraduate nonscience majors. In a prior experiment the students studied additive color mixing using three projectors, with red, green, and blue filters (RGB), respectively, each with variable intensity. The intensity of these RGB lights is measured to determine the RGB components of various colored papers (or of colored plastic filters) illuminated by white light. The goal of that experiment is to analyze how an arbitrary color can be represented by addition of RGB.

In daily life the most common experience of additive color mixing is in the display of colors on TV or computer displays. Irrespective of the display technology (for example, color LCD, plasma screens, digital light processing), these displays are based on closely spaced arrays of RGB colored pixels, sufficiently close that the additive perception of the retina corresponds to the sum of multiple RGB pixels. Subtractive color mixing is encountered primarily in connection with mixing of paints or pigments, be it in the artist’s studio or in magazine or computer printing. The other use of subtractive color mixing is in color photography, where the gamut of colors in slides or motion picture film is produced with mixing of paints or pigments, be it in the artist’s studio or in magazine or computer printing. To analyze the spectral intensity distribution of different colored filters and of paints mixed in different proportions, we use a spectrophotometer connected to a computer, which displays the intensity of diffusely reflected (or scattered) light at each wavelength relative to a predefined white surface. In practice, there is a wide latitude in what people consider a “white surface.” This experiment is possible in an undergraduate teaching lab because miniature-grating spectrophotometers are now commercially available at reasonable cost.

The understanding of color perception and the physical behavior of pigments is complex. For instance, the assumption that yellow paint diffusely reflects primarily yellow wavelengths is incorrect. Rather, the experiments discussed in the following show that yellow reflects a wide range of red and green wavelengths, that is, a significant fraction of the visible spectrum. Similarly, cyan reflects almost all wavelengths in the blue and green spectral regions, and magenta reflects a wide range of blues and reds.

II. EXPERIMENTAL ARRANGEMENT

The experimental arrangement using a commercial spectrophotometer is shown in Fig. 1. A fiber optic probe transmits light reflected from an illuminated sample to a miniature grating spectrometer, which contains a 2048 element linear silicon CCD array in the image plane. The spectrometer is connected to the USB port of a computer, which displays either the spectral distribution of intensity or the reflectance of the surface (percentage reflected relative to a white reference surface) versus wavelength.
The standard reflection/backscattering probe available from the manufacturer contains a bundle of seven closely packed optical fibers: six fibers are coupled to a tungsten light source to illuminate a small area of the sample, while the center fiber transmits the light reflected by the sample to the spectrometer. Our arrangement is different from the commercial one, in that we use an external 20 W halogen lamp to illuminate the sample surface. Furthermore, the fiber bundle is replaced by a single-fiber probe, the probe end of which is protected by a 6 mm diameter stainless steel ferrule. This arrangement has several advantages for student use. The much higher illumination of the sample due to the halogen lamp permits real-time data acquisition free of statistical fluctuations in less than 1 s. Typically we set the acquisition time to 30 ms and average ten spectra. Another advantage of the larger illuminated area is that the surface is readily visible to two or three students in a group.

To study the spectrum of colored filters we provide a simple filter holder, positioned approximately halfway between the lamp and the white surface at the bottom of the box. The only drawback is that even a 20 W halogen bulb is slightly too bright and too hot for our purposes. A heat-absorbing filter was recently added to the filter holder in the lamp to reduce the heat load on the plastic filters.

The box shown in Fig. 1 serves as a mounting surface for the various components and also shields the sample from extraneous room light. The enclosure is made of plywood with interior width of 26 cm, height 28 cm, and depth 17 cm. The inside surfaces are coated with matte black paint.

The orientation of the probe is adjustable. The filter holder swings out of the way when not in use. A slot at the bottom of the rear wall of the box is provided to admit long pieces of paper.
III. SPECTRA OF DIFFERENT LIGHT SOURCES

Students are first asked to record the spectra of different light sources. They place a white sheet of paper underneath the probe and adjust the range of the spectrograph to 400–700 nm. Because LEDs have become common light sources, we have the students inspect the spectra of various LEDs [Fig. 2(a)]. An ulterior motive of this exercise is to reinforce the association of colors (B, G, Y, R) with wavelength regions.

The spectra from other common light sources based on fluorescence and incandescence (thermal emission) are presented in Figs. 2(b) and 2(c). These sources include incandescent and halogen light bulbs, sunlight, and fluorescent light. A comparison of all these spectra with that of an LED white flashlight [Fig. 2(a)] reveals the striking qualitative difference between incandescence [Fig. 2(c)], fluorescence [Fig. 2(b)], and band gap emission in semiconductors [Fig. 2(a)]. In our laboratory the fluorescent light spectrum is easily observed by tilting the box so that the overhead lights illuminate the white paper. If the lab is conducted during daylight hours, observation of natural daylight is also of interest. We either position the box so that sunlight falls on the paper, or we remove the entire stem that holds the probe and point the probe toward the sky.

The spectra in Fig. 2(c) illustrate that the spectrum of sunlight is shifted toward blue compared to that of light bulbs, that is, the sun is hotter than the filaments. Some students will be excited to learn that the dips in the spectrum of the sun give a fingerprint of the elements present on the surface of the sun. Absorption by hydrogen, for example, causes the dips at 657 and 487 nm (H-α and H-β Balmer lines), and the dips near 628 and 686 nm reveal the presence of molecular oxygen Fraunhofer lines.

IV. SUBTRACTIVE COLOR WITH FILTERS

The spectrophotometer can be set up to display the percentage of light reflected from a surface relative to a white surface.

Neutral density gray filters. Students find, as expected, that a gray filter of 50% transmission shows nearly uniform attenuation across the visible spectrum. Observing the spectrum with two such filters leads students to realize that in the subtractive process the transmission is the product of the transmission of the filters: \(0.5 \times 0.5 = 0.25\), rather than the sum of the percentages absorbed.

Sharp-spectrum interference filters. We make use of six filters, three additive primaries, red, green, and blue, and three subtractive primaries, cyan, magenta, and yellow. The corresponding spectra are shown in Fig. 3. In this case, when we add for instance R to B we find zero transmission, that is, black. Similarly, G+R is nearly black. In contrast, combining the subtractive primary filters in pairs yields \(C+Y=G\), \(C+M=B\), and \(M+Y=R\). It thus becomes plausible for students that if we use three subtractive primary filters (or pigments) of different densities, we can produce hues all the way from blue to blue-green to green-yellow, orange, and red.

Colored plastic filters. The filters used in Fig. 3 represent ideal cases. Painted surfaces do not have sharply delineated spectra. Rather, the spectra of reflected light are similar to those of colored semi-transparent plastic film filters. Examples of such filters are presented in Fig. 4. The black curves are the transmittance curves calculated by multiplying the transmittances of the two subtractive-primary filters.

As the density of a filter is increased, the transmittance decreases, making the transmitted light less bright. What is less obvious is that in addition to the change in brightness,
the hue changes, as is illustrated in Fig. 5, which shows the transmittance curve of three identical magenta filters compared to a single filter. Inspection of the light either by eye or by the spectrophotometer immediately shows a striking shift toward red when three filters are used. The explanation is that this particular magenta has a larger transmittance in the red than in the blue, so that after three filters, almost no blue is left. This observation is relevant to photographic color film, in which the color shift caused by incorrect exposure does not simply lighten or darken the image, but changes hues.

V. PIGMENTS

When two paints of different colors are mixed, a third color is obtained, which is different from each of the two components. Can we anticipate what color will result? Artists do so regularly, using their experience; that is, after preparing and seeing many mixtures of different colors, they can remember the resulting colors. We analyze two paints separately and then in a mixture containing both paints. In each case the analysis consists of acquiring the reflectance curve of each color, which is the intensity of light diffusely reflected by the color at each wavelength relative to a white surface.

Mixing of subtractive primaries. In Fig. 6 we present (a) cyan and yellow, which mixed in equal amounts give green, (b) cyan and magenta (give blue), and (c) magenta and yellow (give red). In all these cases there is a change in hue, saturation, and brightness. Also notice that the brightness always decreases in the mixed color, compared with either of the separate colors (with the exception of white, as we will discuss). As seen for overlapping filters, a good approximation of the resulting color can be calculated by multiplying the relative reflectance of the two component colors and rescaling the resulting reflectance curve. (The calculated spectra of Fig. 6 were multiplied by 1.3, 1.3, and 0.9, respectively, to match the experimentally measured spectral intensity.)

Adding white. A white pigment does not absorb light: it scatters light of all wavelengths. Thus, mixing white with any other color adds intensity over the entire spectrum so that the resulting color is lighter, and correspondingly the resulting spectrum is higher in intensity, as shown in the spectra of Fig. 7. For this reason artists often add white to their color mixtures to counteract the loss in brightness due to subtractive color mixing.

Adding white to a paint corresponds to shifting up the off-peak portion of the spectrum (400–550 nm in Fig. 7). Light of wavelengths between 420 and 550 nm is mostly absorbed by red paint. When we add white, part of that light
is diffusely reflected, and correspondingly that portion of the spectrum is raised to a higher intensity (from approximately 15% to approximately 40% in Fig. 7).

Adding black. A vivid demonstration of multiple scattering is provided by the addition of a small fraction (for example, 1%) of black to a colored paint: the result is a much darker color. For example, a small number of black pigments in an orange paint will have multiple chances to absorb light multiply scattered from orange pigments. Each time this orange light meets a black pigment it is absorbed. A small number of black pigments, therefore, have a large effect on the final color of the mixture. In Fig. 8 we show the effect of mixing 1%, 10%, and 50% black to orange acrylic paint. The reflectance curves show that as little as 1% black decreases the brightness by more than 60%.

Additive contribution in mixed paints. Another fundamental mechanism must be taken into account when analyzing the mixing of pigments in paints. There is a small additive mixing component, which is always present, but becomes

Fig. 6. Mixing of (a) equal amounts of cyan and yellow, (b) cyan and magenta, and (c) magenta and yellow give green, blue, and red, respectively. The solid black curves represent the calculated spectra, obtained by multiplying the two component spectra, and rescaling the intensities (Ref. 10).

Fig. 7. The reflectance spectra from white and red paints are shown as black and red lines, respectively. When these two paints are mixed in equal proportions the resulting color is low saturation red, that is, pink (Ref. 11).

Fig. 8. The reflectance curves of orange acrylic paint, black acrylic paint, and mixtures of the two in different proportions (Ref. 12). The mixed volumes were measured using Gilson pipettes and the percentage of black paint is reported for each curve by the right axis.
dominant only when the mixed color is very dark, because the two separate color spectra are far apart, for instance red and blue, as shown in Fig. 9. When mixing these two colors, the resulting color should in principle be black, but instead it is a low intensity purple, with some red light and some blue light additively combined. Red pigments absorb all blue and green from the illuminating white light and diffusely reflect only red light. The reflected red light is in turn almost completely absorbed by nearby blue pigments. Conversely, blue pigments absorb red and diffusely reflect blue. Red and blue pigments, therefore, absorb each other’s reflected light. Near the surface, however, some red and some blue lights escape absorption and are reflected back toward the eye and the spectrophotometer after single scattering by one pigment only, making the mixed color appear purple: the result of red light + blue light in additive color mixing.

Note that in Fig. 9(a) neither the red nor blue paints are saturated, that is, their spectra do not go down to zero intensity in the off-peak region. Consequently, the resulting purple is unsaturated. Similar phenomena are observed in almost all the commercially available paints. In Fig. 8, for instance, the mixtures containing orange paint are unsaturated.

Another phenomenon is illustrated by the data of Fig. 10. Yellow and blue are complementary colors, their spectra should not overlap at all, and their mixture should be black. The Y and B spectra of real pigments, however, have a small region of overlap, in which neither reflectance is zero. The product of the two spectra, therefore, is not black, but has a peak in the green region.

VI. CONCLUSIONS

Our experience is that nonscience students have no difficulty with the use of the spectrophotometer and the associated computer display programs. Students complete most of the experiments presented here in a two-hour laboratory session. Acceptance by the students is uniformly high. These experiments deepen their understanding of subtractive color mixing and lead to an appreciation of the complexity of the phenomena encountered in mixing paints.

The software associated with the commercial spectrophotometer allows the students to display the spectral distribution and, if desired, to overlap a number of spectra for comparison. It is left to students to associate the wavelength scale with the sequence of spectral colors. We have not done so here, but it should be possible to add a band of spectral colors on the computer screen to remind the student to which colors the wavelengths marked on the abscissa correspond.

Hues may be represented in a color triangle such as Maxwell’s color triangle or, more quantitatively, the CIE (Commission Internationale de L’Eclairage) chromaticity diagram. Software is available to display the spectral content acquired by the spectrophotometer as a point in the CIE diagram. Alternatively, the spectral distribution can also be represented as RGB components.

With or without these further refinements, students learn the fundamentals of color and color mixing doing this simple and relatively inexpensive laboratory session. We have tested these experiments on a total of 520 non-science-major students, who invariably enjoyed the lab and described it as a lot of fun. We look forward to hearing from other professors using our experience to implement similar labs at their colleges.

Some additional references to relevant background literature may be useful to the reader less familiar with the subject.
Definitions: Given any color, a matching color that appears to the normal retina identical to the color in question, can always be obtained by combining light of a single wavelength with white light (except for magentas and purples, which are specified by the complementary wavelength). The wavelength of the matching color is called the dominant wavelength. The corresponding attribute of visual sensation is called the hue. The fraction of white light is called saturation. Saturation is also known as purity. High saturation colors require a small percentage of white in the matching color, low saturation colors require a large percentage of white. These are pale pink, sky blue, pale yellow, beige, and all colors commonly called pastels. The adjectives saturated and pale are therefore antonyms. To match those colors, the matching color requires a large fraction of white. Some authors define saturation in paints and pigments to be the parameter related to the amount of black, but we do not see a reason for such distinction. Brightness (also known as lightness) is the parameter of a color according to which an area appears to emit more or less light. The adjectives bright and dark (or light and dark) are therefore antonyms. In the literature there is a preference to use the term brightness for luminant sources, and lightness for illuminated surfaces. Different color systems (Munsell, Oswald, and DIN) use other terms (for example, value, chroma), but for simplicity we use terminology familiar from everyday English.


THE ARGUMENT FROM PERSONAL INCREDULITY

“The human journey to cosmic space and time was bedeviled at every step of the way by what the biologist Richard Dawkins calls the Argument from Personal Incredulity: If it seems impossible to believe, it must be wrong. Aristarchus confronted the incredulity of his contemporaries, as did Copernicus, Bruno, Galileo, and Darwin. The universe invariably turned out to be bigger and older than we had previously thought possible. The light-years and the eons are a tribute to the power of the boldest, most daring human thinkers to transcend ‘common sense.’”