Robert T. Marcus. "Colorimetry."

Colorimetry

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58.1 Introduction

Imagine how dull a world without color would be. Until the 1960s, many products were available in only a limited variety of colors. Consumers demand a variety of colors, and the materials available today allow manufacturers to meet those demands.

For many centuries, color was controlled by master color matchers adjusting the color of their products visually in natural daylight. It was about the 1950s when color measuring instruments began to make a significant impact in the manufacturing process, and by the 1970s they were commonly used in most industries. Color measuring instruments are used mostly for quality control but also for computerized color matching systems, process control, evaluation of raw materials, and as an aid to solving color problems.

While it is common to speak of a red car or a red light, color is a perception—not an intrinsic property of the object or the light. Color perception is influenced by the light source, the reflectance or transmittance properties of the object, the eye, and the brain. Color is one aspect of appearance. Gloss and texture are other aspects.

Color perception is three dimensional, i.e., three terms are needed to describe a color. Hue, lightness (sometimes called value), and chroma are one set of terms often used to describe color. Hue distinguishes blue from green from yellow, etc. Lightness distinguishes light colors from dark colors—for example, a light blue fabric from a dark blue fabric. Chroma, the most difficult of the three terms to understand, describes how different a color is from gray—for example, distinguishing a pastel green from a bright green. If the two greens are of the same hue (one is neither yellower nor bluer than the other) and have the same lightness, then the pastel green would be described as having a low chroma and the bright green as having a high chroma. Figure 58.1 is a diagram illustrating the three dimensions of color.

Daylight, fluorescent lamps, and incandescent lamps are widely used light sources for color evaluation. The perceived color of an object changes as the light changes. The human visual systems attempt to compensate for the change in light source and hold the color constant. Light booths provide standardized and controlled light sources for the visual evaluation of color. Most light booths contain a simulated daylight lamp, a cool white fluorescent lamp, an incandescent lamp, and an ultraviolet lamp for detecting fluorescence. By use of a switch, a light booth can be used to examine how the perception of a colored material changes with different light sources.

Two objects may appear the same when viewed under one light source, but different when viewed under another light source. This effect, called metamerism, is one of the major industrial problems for color matching. Metamerism usually occurs when attempts are made to produce objects that are the same color but made out of different materials, such as trying to match the dyed textile interior of a car with paint on the exterior and the plastic on the dashboard.

Colorimetry, the measurement of color, attempts to quantify the perception of color. The Commission Internationale de l'Éclairage (International Commission on Illumination, or CIE) is a voluntary organization of scientists and engineers from all over the world who are interested in light and color. The recommendations constituting modern colorimetry were first published by the CIE in 1931 and have been regularly updated since then [1].

Electromagnetic radiation (x-rays, gamma rays, light, and radio waves) irradiates the Earth constantly. Visible light is the name given to the electromagnetic radiation that the human eye perceives. The wavelength of visible light ranges from about 380 nm to about 780 nm. Sunlight is a mixture of all the wavelengths of light. Water vapor can spatially separate the light into its various wavelengths—the rainbow. Prisms and diffraction gratings can also spatially separate light into its component wavelengths.

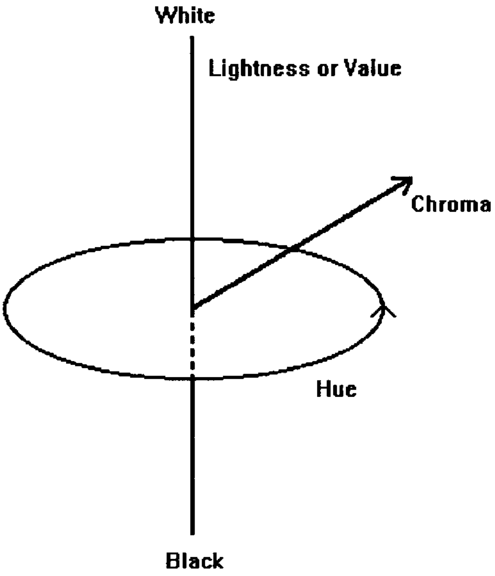

FIGURE 58.1 The three dimensions of color.

Light sources can be described numerically by their spectral power distribution, the relative amount of power the source emits at each wavelength of interest. A light source may emit power at wavelengths below (ultraviolet "light") or above (infrared "light") those of visible light. Ultraviolet radiation is important to colorimetry because it can cause fluorescence. Infrared radiation is the basis of "heat lamps" but is not important in colorimetry. Spectroradiometers measure the spectral power distribution of light sources.

Illuminants and sources are sometimes confused. Sources are actual physical entities that produce visible radiation, whereas an illuminant may only be a numerical table of values of a spectral power distribution. Initially, the CIE recommended three light sources for colorimetry in 1931. Source A, which is still in use, is an incandescent, tungsten filament light. An illuminant is the spectral power distribution of a light source. Thus, Illuminant A is the spectral power distribution of Source A. An illuminant may be defined, even when a source for that illuminant does not exist. Examples of illuminants without sources are the D series of illuminants recommended by the CIE. The D illuminants represent various phases of daylight. Illuminant D65 represents average daylight and is the most common illuminant used in colorimetry. No sources were recommended for the D series of illuminants.

Fluorescent lights have great commercial importance. Cool white fluorescent lamps are the most common light sources in offices in the United States. There are a variety of other types of fluorescent lamps used in stores and offices. The CIE also recommended a series of illuminants to represent fluorescent lamps. F2 represents cool white fluorescent lamps. Figure 58.2 shows the spectral power distributions of Illuminants A, D65, and F2.

Color vision and perception is complex and has been extensively studied. Ninety-two percent of men and 99.5 percent of women have "normal" color vision. The eye's lens focuses images on the light-sensitive retina. Rod cells make up the majority of the retina and are sensitive to low levels of illumination (night vision). Cone cells provide color vision and are located in a small area of the retina called the *foveal pit.* There are three types of cone cells. One type of cone cell has peak sensitivity to blue light, one type to green light, and one type to red light. Signals from the cone cells are transmitted to the brain where they are processed into color perceptions.

Color perception is an extremely complex phenomenon. For example, the background on which a material is viewed can have a major effect on the perceived color of that material. The ambient light to which the eye becomes adapted also influences the color of materials. Basic colorimetry, the topic of this chapter, provides the rather simple concept of dealing with the measurement of single independent colors. Most of industrial color control is adequately described using basic colorimetry. Advanced colorimetry attempts to use physical measurements to describe the perceived color of a material when viewed in a complex scene.

All colors are perceived by stimulating combinations of the three cones. Computer monitors and color television tubes produce colors by lighting combinations of red, green and blue phosphors. In 1931 when

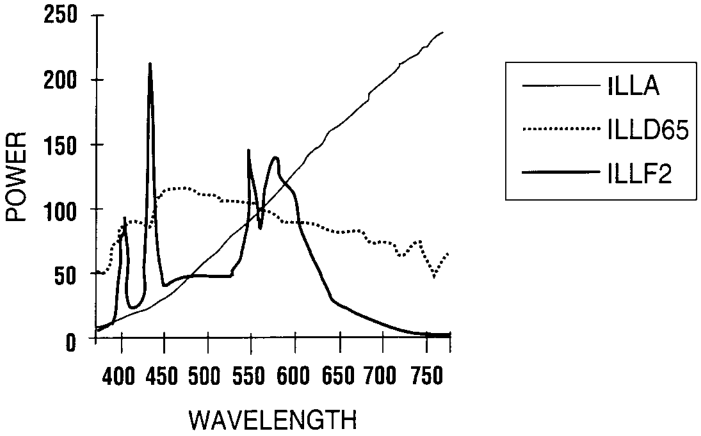

FIGURE 58.2 The spectral power distribution of CIE Standard Illuminants A, D65, and F2.

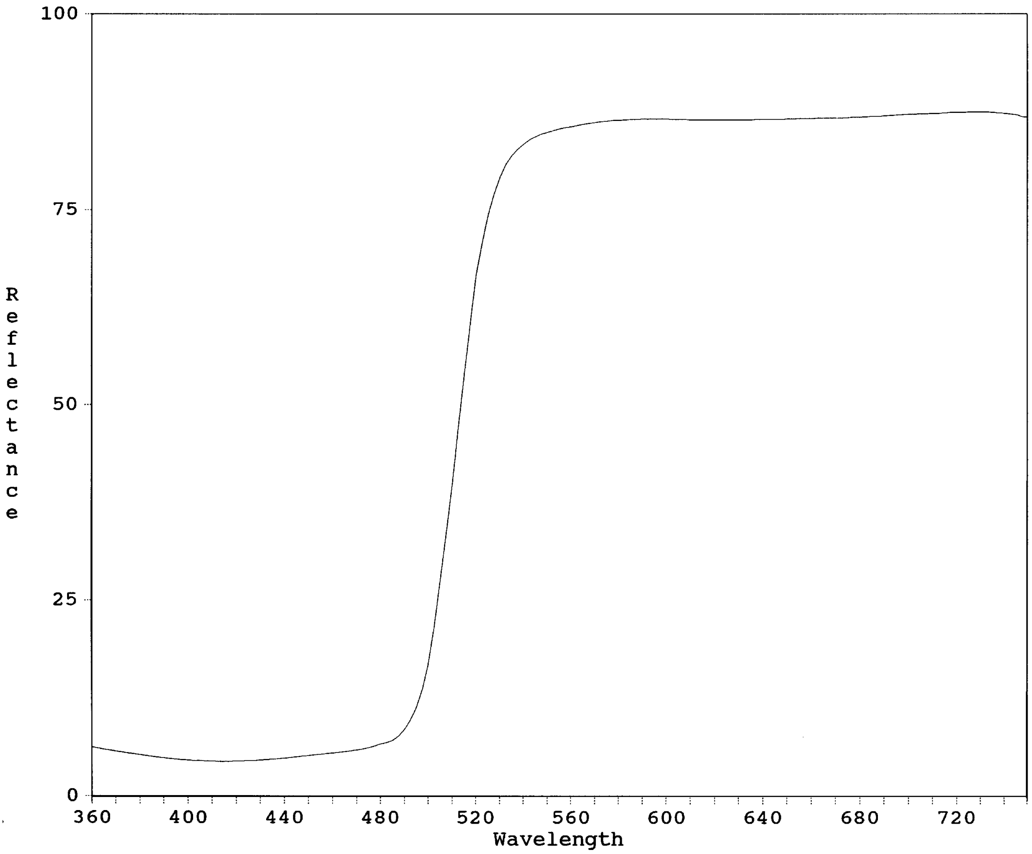

FIGURE 58.3 The spectral reflectance curve of a printed yellow ink.

the CIE was developing the system for modern colorimetry, they transformed the data from real experiments that had human observers match each wavelength of visible light with combinations of red, green and blue lights, to three mathematical imaginary "lights" labeled X, Y, and Z. All colors can be matched by varying amounts of X, Y, and Z. The amounts of each X, Y, and Z imaginary light that must be mixed together to match a color are called the tristimulus values (see "The CIE Standard Observers," page 58-6).

Most objects absorb, transmit, or reflect (scatter) light. Transparent objects absorb and transmit light. Opaque objects absorb and reflect light. Light sources emit light. Fluorescent objects absorb, reflect, and emit light. Translucent or hazy objects absorb, transmit, and scatter light. Measuring the color of fluorescent, translucent, and hazy objects is difficult and will be covered in later sections.

Objects are characterized by the amount of light they reflect or transmit at each wavelength of interest. Most spectrophotometers measure reflectance factors rather than reflectance. Reflectance is the amount of light reflected from an object compared to the amount of light illuminating that object. The reflectance factor is the amount of light reflected from an object compared to the amount of light reflected from a perfect diffuser under the same conditions. A perfect diffuser is a theoretical material that diffusely reflects 100 percent of the light incident upon it. The term reflectance is often used in a general sense, or as an abbreviation for, reflectance factor. Such usage may be assumed unless the term reflectance is specifically required by the context [49]. Spectrophotometers designed for color measurement usually measure reflectance or transmittance at 10- or 20-nm intervals throughout the visible spectrum.

When the reflectance or transmittance of an object is low, the object absorbs most of the incident light; when it is high, the object reflects or transmits most of the incident light. Figure 58.3 shows the reflectance curve of a printed yellow ink. Note that the yellow ink absorbs light in the blue portion

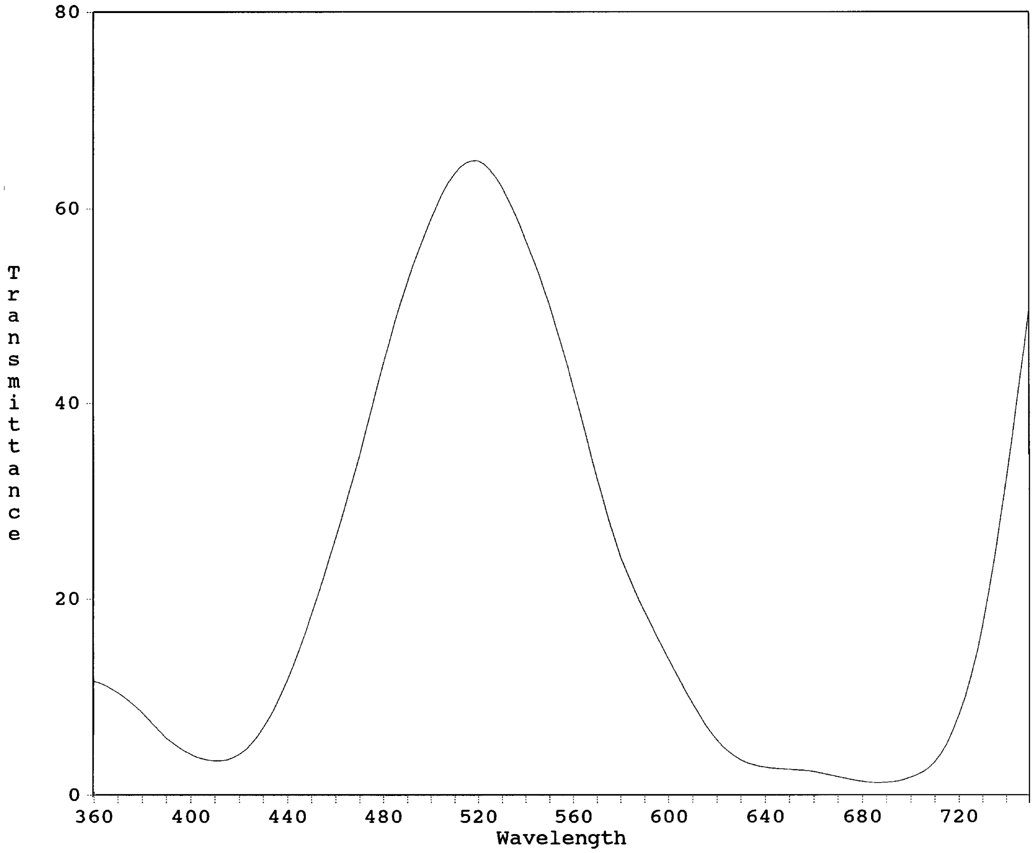

FIGURE 58.4 The spectral reflectance curve of a green transparent plastic.

of the spectrum and reflects light in the yellow and red portions of the spectrum. A green plastic (Figure 58.4) absorbs light in the blue and red portions of the spectrum and transmits light in the green portion.

The tristimulus values of an object can be calculated by combining the reflectance or transmittance of the object with the spectral power distribution of an illuminant and the color matching functions of a Standard Observer. The yellow ink's tristimulus values for Illuminant D65 and the 10 Degree Standard Observer are X = 66.62, Y = 69.72, and Z = 7.03. Those for the green plastic are X = 21.03, Y = 39.40, and Z = 24.06. An object's tristimulus values will change with the illuminant. For example, the tristimulus values for the yellow object for Illuminant A and the 10 Degree Standard Observer are X = 91.15, Y = 77.83, and Z = 2.80.

Pairs of objects are said to match when their tristimulus values are the same. However, since the calculation of the tristimulus values included the source and observer as well as the object, when one of these changes, the objects may no longer match, i.e., they may have different tristimulus values. Metameric colored objects have the same tristimulus values for the illuminant under which they match but different tristimulus values for illuminants where they do not match.

Color measurements are most often made to determine quantitatively whether or not the colors of two objects or batches of material are the same. But what happens when they do not match? Color difference equations were developed to quantify the difference. Starting with the objects' tristimulus values, a color difference equation will calculate the total color difference, ΔE or DE, and its component parts—the differences in lightness (ΔL or DL), chroma (ΔC or DC) and hue (ΔH or DH) or the differences in lightness, yellowness-blueness (Δb or Db) and redness-greenness (Δa or Da). Numerical color differences may be used for setting tolerances for quality control applications, to answer the question: is the match close enough?

58.2 Standardized Light Sources

Color Temperature

Light sources may be described by their color temperature. A block of carbon would look completely black when its temperature was at absolute zero, 0 K. When the carbon block is heated to about 2850 K, it looks yellow—about the same color as an incandescent light bulb. Heat the block to 5000 K, and it looks whitish. At 7500 K, the block would have the bluish color of north sky daylight. A full (blackbody) radiator is a theoretically perfect emitter and absorber of radiation that changes color like the carbon block just described. The color temperature of a light source is the temperature of a full radiator that has the same color as the light source. When a light source does not exactly match the color of a full radiator, the correlated color temperature is used to describe the light source. The correlated color temperature is the temperature of a full radiator whose color is closest to the source.

Daylight varies during the day—redder in the morning and evening and bluer at noon. Average daylight (diffuse skylight without direct sunlight) has a color temperature of 6500 K. North sky daylight is preferred by many people for the visual evaluation of color and has a color temperature of 7500 K.

CIE Recommendations

Source A has a color temperature of 2856 K. The CIE recommended daylight illuminants are referred to by the prefix D, followed by the first two digits of their color temperature. Thus, CIE Illuminant D65 has a color temperature of 6500 K. Illuminant D50 has a color temperature of 5000 K and is preferred by the graphic arts community. Illuminant D75 would be used for north sky daylight having a color temperature of 7500 K. Illuminant F2 has a color temperature of about 4100 K.

58.3 The CIE Standard Observers

The CIE adopted two Standard Observers based on color matching experiments. The CIE 2 Degree Standard Observer was recommended in 1931, and the CIE 10 Degree Standard Observer was recommended in 1964.

In the CIE experiments, observers having normal color vision matched spectrum colors with combinations of red, green, and blue light. Figure 58.5 illustrates the experimental setup used in the Standard

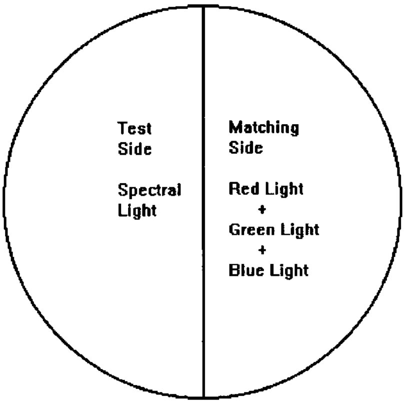

FIGURE 58.5 Experimental field of view for determining the CIE Standard Observers.

Observer experiments. One-half of a circular field was illuminated with the spectrum color, while the other half was illuminated with a mixture of red, green, and blue lights. The observer adjusted the amounts of red, green, and blue until the mixture matched the spectrum color. Unfortunately, not all of the spectrum colors could be matched with combinations of the red, green, and blue lights used in the experiment. In those cases, one of the lights had to be moved so that it illuminated the test field. By "diluting" the spectrum color with one of the lights, the resultant color could be matched with the remaining two lights. The amount of light used to dilute the spectrum color was considered to be a negative amount. To avoid having color matching functions with negative amounts of light, three "imaginary" lights (X, Y, and Z) were created by performing a mathematical transformation. Color matching functions are the amounts of X, Y, and Z required to match the colors of the spectrum and are used in the calculation of tristimulus values. Figure 58.6 shows the color matching functions, ($\bar{x}$, $\bar{y}$, and $\bar{z}$) for the 10 Degree Standard Observer.

In the first experiments, the circular field viewed was projected on the foveal pit and subtended a solid angle of 2°. This is about the size of a dime held at arm's length. The 2 Degree Standard Observer developed from these experiments is very useful when viewing small fields, such as the signal lights of ships or small colored chips. Industrial color matchers view larger fields, such as two 5 × 12-inch panels. The 10 Degree Standard Observer should be used when viewing larger fields. Observers for those experiments viewed a 10° visual field, which is about the size of a fist held at arm's length.

The standard observers represent combinations of the color matching functions of a number of observers. Standard observer color matching experiments are tedious and difficult to do. Few people can do them with reproducibility. An individual's color matching functions are likely to vary from that of a CIE Standard Observer. Although these differences do not generally present a problem, they can affect the evaluation of metameric samples.

58.4 Calculating Tristimulus Values

Tristimulus values for a reflecting samples are calculated from the following equations:

$$X = k \int_{380}^{780} R_\lambda S_\lambda \bar{x}_\lambda d\lambda \cong k \sum_{380}^{780} R_\lambda S_\lambda \bar{x}_\lambda \Delta\lambda \tag{58.1}$$

$$Y = k \int_{380}^{780} R_\lambda S_\lambda \bar{y}_\lambda d\lambda \cong k \sum_{380}^{780} R_\lambda S_\lambda \bar{y}_\lambda \Delta\lambda \tag{58.2}$$

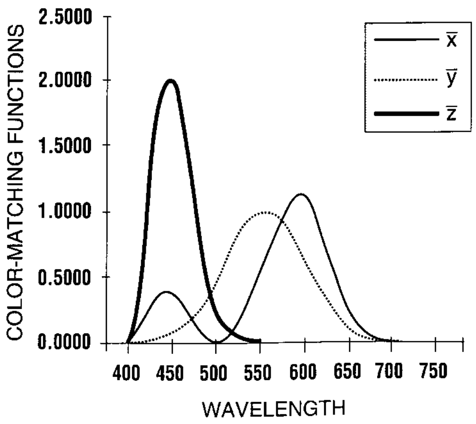

FIGURE 58.6 The color matching functions for the CIE 10 Degree Standard Observer.

$$Z = k\int_{380}^{780} R_\lambda S_\lambda \bar{z}_\lambda d\lambda \cong k\sum_{380}^{780} R_\lambda S_\lambda \bar{z}_\lambda \Delta\lambda \tag{58.3}$$

$$k = \frac{100}{\int_{380}^{780} S_\lambda \bar{y} d\lambda} \cong \frac{100}{\sum_{380}^{780} S_\lambda \bar{y} \Delta\lambda} \tag{58.4}$$

in which S_λ is the relative spectral power distribution of the illuminant at wavelength λ, R_λ is the reflectance factor of the sample at wavelength λ, and $\bar{x}_y$, $\bar{y}_\lambda$, and $\bar{z}_\lambda$ are the color matching functions of the observer at wavelength λ. For transmitting objects, substitute the transmission factor, T_λ, of the sample at wavelength λ for the reflectance factor. The factor k normalizes Y so that it will equal 100.00 for a perfect reflector or transmitter, i.e., R_λ or T_λ is 100.00 at all wavelengths of interest. The summations in the above equations are only valid if the reflectance or transmittance of the sample is measured at wavelength intervals of 1 nm or 5 nm from 380 to 780 nm.

Many commercial spectrophotometers measure wavelength intervals of 10 or 20 nm. To accurately calculate tristimulus values of samples measured with those instruments, the following equations should be used:

$$X = \sum W_{x\lambda} R_\lambda \tag{58.5}$$

$$Y = \sum W_{y\lambda} R_\lambda \tag{58.6}$$

$$Z = \sum W_{z\lambda} R_\lambda \tag{58.7}$$

in which $W_{x\lambda}$, $W_{y\lambda}$, and $W_{z\lambda}$ are weighting factors designed for 10 and 20 nm wavelength intervals. T_λ can be substituted for R_λ for transmitting samples. Although a number of weighting factors have been developed over the years [2–7], those recommended by ASTM in E 308 Standard Practice for Computing the Colors of Objects by Using the CIE System [7] are recommended.

Tristimulus values for a light source can be calculated easily from measurements taken at 1 or 5 nm intervals from the following equations:

$$X = \frac{k_m}{\sum \bar{y}_\lambda} \sum S_\lambda \bar{x}_\lambda \tag{58.8}$$

$$Y = \frac{k_m}{\sum \bar{y}_\lambda} \sum S_\lambda \bar{y}_\lambda \tag{58.9}$$

$$Z = \frac{k_m}{\sum \bar{y}_\lambda} \sum S_\lambda \bar{z}_\lambda \tag{58.10}$$

in which S_λ is the relative spectral power of the light source at wavelength λ, k_m is the maximum spectral luminous efficacy function (683 lm W^{-1}), and $\bar{x}_y$, $\bar{y}_\lambda$, and $\bar{z}_\lambda$ are the color matching functions for the standard observer.

58.5 Reflectance Measurements

Specular and Diffuse Reflectance

Specular (sometimes called *regular*) reflection is the mirror-like reflection from an object. If you shine a beam of light on a mirror, it will be entirely reflected at the same angle on the opposite side of a normal plane to the mirror's surface. However, if you shine a beam of light on a pellet of compressed barium sulfate ($BaSO_4$) powder, it will enter the surface, be scattered a number of times, and exit the pellet in many directions. This is called diffuse reflection. Glossy and semiglossy materials contain a combination of specular and diffuse reflection as shown in Fig. 58.7. Observers usually discount the specular reflection when visually evaluating the color of a material.

Illuminating and Viewing Geometries for Reflectance

Instruments designed for measuring the color of reflecting objects consist of an illuminator, a sample holder, and a receiver. The CIE has recommended four illuminating and viewing geometries for making reflectance measurements.

Bidirectional geometries illuminate the sample with a narrow beam of light and view the sample with a receiver having a narrow entrance field. In the most commonly used bidirectional geometry, the sample is illuminated at a 45° angle (±2°) from the sample's normal and viewed along the sample's normal (±10°). The other recommended geometry illuminates the sample along its normal and views the sample at 45° from its normal. Bidirectional geometries measure only diffuse reflection and can be sensitive to the surface texture of the sample. The two bidirectional geometries produce equivalent results [8, 9].

In the most common diffuse geometry, the illuminator includes an integrating sphere. An integrating sphere is a hollow metal sphere coated with a highly reflecting white coating with openings for the light source, the sample, and the receiver. The instrument's light source projects a beam of light onto the integrating sphere's wall. The light is reflected many times by the sphere's wall, and the sample is illuminated from all angles. When measuring in the diffuse/normal mode, d/0, the receiver views the sample along its normal. When the receiver is positioned in this manner, the specular reflection is directed back towards the light source and is not measured.

For some applications, it is useful to remove the specular reflection off of the sample's surface from the reflection of the light that is reflected back from the interior of the sample. This can be done by moving the receiver 6 or 8° from the sample's normal as shown in Fig. 58.8. A specular inclusion port is placed at the equal angle on the opposite side of the sample's normal. By placing a white plug having the same reflectance as the sphere wall in the port, the specular reflection can be included in the measurement. By using a light trap at the specular inclusion port, some or all of the specular reflection can be excluded from the measurement. The narrower the specular reflection peak, i.e., the glossier the material, the more specular reflection is excluded. Specular included measurements are normally abbreviated SCI, while specular excluded measurements are abbreviated SCE. This geometry is referred to as diffuse/near-normal but still abbreviated d/0. When the specular reflection is included, this geometry is sometimes referred to as total/normal, t/0.

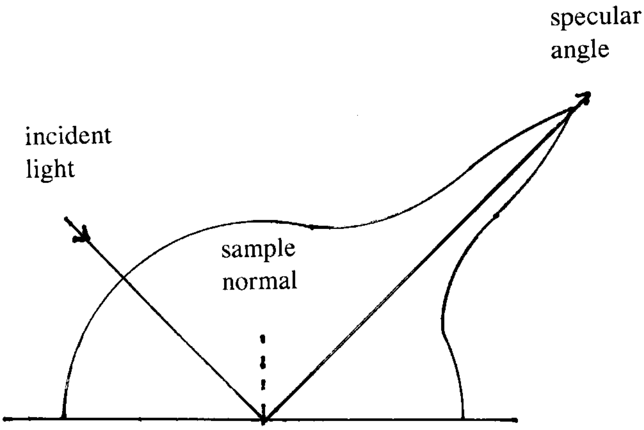

FIGURE 58.7 A semiglossy material showing a combination of specular and diffuse reflection.

The last of the CIE recommended illuminating and viewing geometries is the normal/diffuse or near-normal/diffuse, 0/d and 0/t. This is the reverse of the d/0 geometry. The illuminator illuminates the sample along its normal, or slightly off of its normal. For this geometry, the integrating sphere is part of the receiver. Light reflected from the sample is captured by the integrating sphere and the remaining optics of the receiver views the sphere wall. The two diffuse geometries produce equivalent results [8, 9].

Monochromatic and Polychromatic Illumination

An instrument's illuminator may illuminate the sample with either a narrow band of wavelengths, 1 to 10 nm wide, called monochromatic illumination, or a wide band of wavelengths, usually simulating a daylight illuminant and called polychromatic illumination. For nonfluorescent samples, either illumination method can be used with equivalent results. However, for fluorescent samples, only polychromatic illumination can produce valid results.

Sample Texture and Bidirectional Geometries

Bidirectional illuminating and viewing geometries can be very sensitive to surface texture and any polarization of reflected light. Keeping the illuminator and receiver in the same plane maximizes this sensitivity. To reduce or eliminate this sensitivity, circumferential or annular illumination (or receiving) can be used. When an illuminator provides light (or the receiver possesses responsivity) at many points distributed uniformly around a 45° cone centered at the sample's normal, we refer to circumferential illumination (or viewing). When the illuminator provides light continuously and uniformly around the cone, we refer to annular illumination (or viewing).

Which Illuminating and Viewing Geometry Is Best?

"Which illuminating and viewing geometry is best for color measurement?" is a difficult question to answer [9–12]. For matte samples, all of the geometries produce equivalent results. For high-gloss samples, the diffuse geometries with the specular reflection excluded provide measurements very close to the bidirectional geometries. For semigloss samples, the problem becomes more complex. The two bidirectional geometries are similar to the way a person evaluates color visually and are often thought

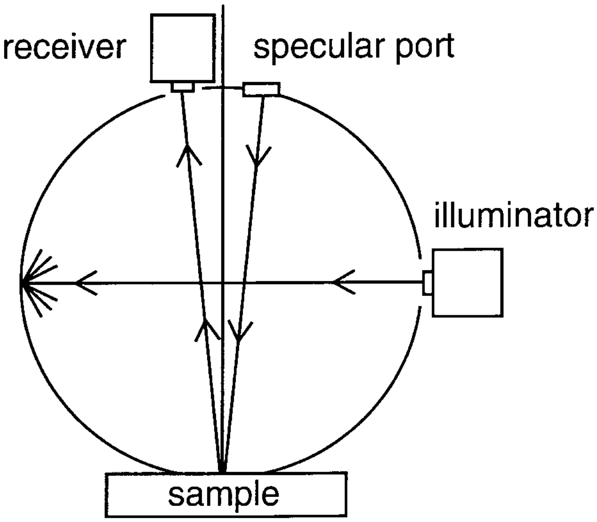

FIGURE 58.8 The diffuse/normal illuminating/viewing geometry with the ability to include or exclude the specular surface reflection.

to agree better with visual evaluation. On the other hand, the diffuse geometries measured with the specular reflection included minimize the effect of the sample's texture and gloss and are quite useful for computerized color matching. Rather than purchasing multiple instruments, most users select the geometry most suited to their major needs and compromise on other measurements.

Spectrophotometers

Spectrophotometers are used to measure an object's reflection characteristics throughout the visible spectrum. Double-beam spectrophotometers monitor a reference standard to compensate dynamically for fluctuations in source output, detector response, and atmospheric absorption to increase the instrument's stability [13]. Improvements in electronics and optics have allowed single-beam spectrophotometers to achieve the stability of double-beam instruments [14]. Single-beam instruments with an integrating sphere require a correction for the reduction of sphere efficiency caused by sample absorption [14].

Reflectance measurements are referred to as if they take place at a single wavelength. In actuality, a spectrophotometer has a finite spectral bandwidth or bandpass centered about that wavelength. Some instruments will have a bandpass as narrow as 1 nm, while others may exceed 20 nm. Bandpass is important because it influences the color measurement. The extent of this influence depends on the sample being measured [15, 16]. The spectral bandpass should be equal to the wavelength increment used in the calculation of tristimulus values to obtain the best color measurement results [17].

Spectrophotometers must be standardized before making reflectance factor measurements. The high point of the measurement scale is set by measuring a white standard of known reflectance factor [18]. The zero point is set by measuring a light trap or a black calibration standard. Single-beam, integrating sphere spectrophotometers may also require a sphere wall calibration, which is often done with a gray standard.

Some spectrophotometers allow the user to vary the size of the area measured. For most applications, the largest area possible should be measured. A number of documentary standards exist for making and reporting reflectance measurements [9, 17, 19-25].

Colorimeters and Spectrocolorimeters

Colorimeters were developed in the 1920s to 1930s as a less expensive alternative to spectrophotometers for quality control and color difference applications. They are simple to use and directly measure a sample's tristimulus values or related color coordinates. Three or four filters modify the light source and attempt to duplicate a Standard Illuminant/Standard Observer combination. Because of the difficulty in matching the CIE Illuminant and Standard Observer functions, they are less accurate than spectrophotometers for determining a sample's tristimulus values. Colorimeters determine the color difference between two samples more accurately than they determine tristimulus values, and they are often called color-difference meters. Since only one Standard Illuminant/Standard Observer combination is usually possible, colorimeters cannot be used to determine metamerism. Standards also exist for making colorimeter measurements [24–26].

A new class of instruments, spectrocolorimeters, began to appear in the 1980s. Spectrocolorimeters are spectrophotometers that only output tristimulus values or related color coordinates. They are less expensive and often have fewer options (such as variable area of view) than fully functional spectrophotometers. However, because they are spectrophotometers, they are capable of measuring metamerism.

Sample Preparation

Accurate color measurement is often dependent on sample preparation. Ideally, a sample for reflectance measurement is flat, has a uniform gloss and texture, is opaque, and is nondirectional. Always strive for sample preparation techniques that are reproducible. Consult standard test methods [24], standard practices [19, 27–29], books and articles [30–33] for help and advice on sample preparation.

58.6 Transmittance Measurement

Regular and Diffuse Transmittance

When a beam of light passes through a "transparent" material along its normal, the intensity of the beam will be decreased by absorption, but the direction of the beam will be unchanged. This is called regular transmittance. When a beam of light passes through a hazy or translucent material along its normal, the material scatters light and spreads the beam. This is called diffuse transmittance.

Illuminating and Viewing Geometries for Transmittance

The CIE has recommended three illuminating and viewing geometries for transmittance measurements. [1] Most transmittance measurements are made with spectrophotometers designed for analytical chemistry applications that use a normal/normal, 0/0, geometry. The illuminator directs the incident beam along the sample's normal, and the receiver views the sample along its normal. Only regular transmittance can be measured accurately using this geometry.

Regular and diffuse transmittance can be measured using the normal/diffuse, 0/d, geometries (or the equivalent diffuse/normal, d/0), which the CIE also recommended for reflectance measurements. Regular transmittance is measured by keeping the sample as far away as possible from the integrating sphere, whereas diffuse transmittance is measured by placing the sample in contact with the sphere. Instruments designed specifically for transmittance measurements would have only a sample or illuminator port and a receiver port. Instruments designed for reflectance measurements can be used for making transmittance measurements by placing a white material in the sample port and using the specular included mode of measurement. The illuminator or receiver port would then serve as the sample port.

The third geometry recommended by the CIE, diffuse/diffuse, d/d, is not often used for industrial color measurement. One integrating sphere is used to illuminate the sample, and a second integrating sphere is used to view the sample.

The two bidirectional reflectance geometries (45/0 and 0/45) have also been used for making regular transmittance measurements.

Monochromatic and Polychromatic Illumination

Instruments for measuring transmittance may have either monochromatic or polychromatic illumination. The transmittance of nonfluorescent samples can be measured using either type of illumination, but fluorescent samples can only be measured using polychromatic illumination.

Standardizing Instruments for Transmittance Measurements

Three techniques exist for setting the high end of the measurement scale, a transmittance factor of 1.0. Each technique produces different results, so it is important to document the method used.

Setting the instrument to read a transmittance factor of 1.0 with no sample in the sample compartment is the easiest technique. The transmittance measurements will then be relative to air. This technique is often used when solid samples are being measured.

Transmittance measurements of solid materials may also be made relative to a clear blank of similar material. To make these measurements, the clear blank is placed in the sample compartment before the instrument is standardized.

When liquids are to be measured, a holder containing solvent or nonabsorbing liquid of the same refractive index as the liquid to be measured should be placed in the sample compartment before standardizing the instrument. This eliminates any effects of the holder's transmittance.

Sample Preparation

Ideal samples will be flat with parallel sides. Liquid sample holders should be made from optical glass. Because transmittance will change with sample thickness and the concentration of colorant, it is important that sample holders and blanks used for standardization have the same path length or thickness as the sample. When two different samples must be compared, they should be prepared using the same technique and have the same thickness.

It is extremely difficult to measure the transmittance of curved materials because the curvature of the object may act as a lens and deflect the incident light away from the receiver. If the curvature is not too great, it may be possible to make a diffuse transmittance measurement.

58.7 Color Difference Calculations

A number of equations have been developed over the years for calculating the color difference between two objects [1, 10, 24, 30, 34, 35, 36]. One of the most common equations is the CIELAB recommended by the CIE in 1976 [1].

First the CIELAB coordinates, L^* (lightness), a^*, b^*, C^*_{ab} (chroma) and h_{ab} (hue angle) are calculated with Equations 58.11 through 58.15.

$$L^* = 116\, f(Y/Y_n) - 16 \tag{58.11}$$

$$a^* = 500\, [f(X/X_n) - f(Y/Y_n)] \tag{58.12}$$

$$b^* = 200\, [f(Y/Y_n) - f(Z/Z_n)] \tag{58.13}$$

$$C^*_{ab} = [a^{*2} + b^{*2}]^{1/2} \tag{58.14}$$

$$h_{ab} = \arctan[b^*/a^*] \tag{58.15}$$

in which X, Y, and Z are tristimulus values and the subscript n refers to the tristimulus values of the perfect diffuser for the given illuminant and standard observer; $f(X/X_n) = (X/X_n)^{1/3}$ for values of (X/X_n) greater than 0.008856 and $f(X/X_n) = 7.787(X/X_n) + 16/116$ for values of (X/X_n) equal to or less than 0.008856; and the same with Y and Z replacing X in turn. The hue angle is 0° along the $+a^*$ axis, 90° along the $+b^*$ axis, 180^0 along the $-a^*$ axis, and 270^0 along the $-b^*$ axis.

The total color difference, ΔE^*_{ab}, and its components—the lightness difference, ΔL^*, the chroma difference, ΔC^*_{ab}, and the hue difference, ΔH^*_{ab}—are calculated using Equations 58.16 through 58.21.

$$\Delta L^* = L^*_{\text{trial}} - L^*_{\text{standard}} \tag{58.16}$$

$$\Delta a^* = a^*_{\text{trial}} - a^*_{\text{standard}} \tag{58.17}$$

$$\Delta b^* = b^*_{\text{trial}} - b^*_{\text{standard}} \tag{58.18}$$

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{58.19}$$

$$\Delta C^*_{ab} = C^*_{\text{ab trial}} - C^*_{\text{ab standard}} \tag{58.20}$$

$$\Delta H^*_{ab} = [(\Delta E^*_{ab})^2 - (\Delta L^*)^2 - (\Delta C^*_{ab})^2]^{1/2} \tag{58.21}$$

A negative value of ΔL^* means the trial is darker than the standard, and a negative value of ΔC^*_{ab} means the trial has a lower chroma than the standard. When the hue angle, h_{ab} of the trial is greater than that of the standard, the sign of ΔH^*_{ab} is positive, and vice-versa. The total color difference and its components can then be used in setting color tolerances [19, 37].

Researchers have been making modifications to the CIELAB color difference equation in an attempt to have the color difference more closely correlate with visually observed color differences. The CMC(*l*:*c*) color difference equation [50–52] has gained great acceptance in the textile industry and is being tested in other areas. Starting with the CIELAB color differences, the CMC(l:c) color differences are calculated with Equations 58.22 through 58.28.

$$\Delta E = \left[\left(\frac{\Delta L^*}{lS_L}\right)^2 + \left(\frac{\Delta C^*_{ab}}{cS_C}\right)^2 + \left(\frac{\Delta H^*_{ab}}{S_H}\right)^2\right]^{1/2} \tag{58.22}$$

$$S_L = \frac{0.040975L^*}{1 + 0.01765L^*} \tag{58.23}$$

unless $L^* < 16$, in which case $S_L = 0.511$,

$$S_C = \frac{0.0638C^*_{ab}}{1 + 0.0131C^*_{ab}} + 0.638 \tag{58.24}$$

$$S_H = (FT + 1 - F)S_C \tag{58.25}$$

$$F = \left(\frac{(C^*_{ab})^4}{(C^*_{ab})^4 + 1900}\right)^{1/2} \tag{58.26}$$

$$T = 0.36 + \text{abs}[0.4\cos(35 + h_{ab})] \tag{58.27}$$

unless h is between 164° and 345° when

$$T = 0.56 + \text{abs}[0.2\ \cos(168 + h_{ab})] \tag{58.28}$$

in which the notation "abs" indicates the absolute (i.e., positive,) value of the term inside the square brackets. When $l = c = 1$, the formula quantifies the perceptibility of color differences. Optimum values of l and c for quantifying the acceptability of a color match must be determined for the material being measured. The textile industry has found the optimum values to be $l = 2$ and $c = 1$ [51].

In 1994, the CIE recommended a new color difference equation, CIE94 [36], which is similar to the CMC equation. CIE94 color differences are calculated using Equations 58.29 through 58.33. The perceived color-difference, ΔV, is related to the measured color difference through an overall sensitivity factor, k_E.

$$\Delta V = \frac{1}{k_E}\Delta E^*_{94} \tag{58.29}$$

$$\Delta E^*_{94} = \left[\left(\frac{\Delta L^*}{k_L S_L}\right)^2 + \left(\frac{\Delta C^*_{ab}}{k_C S_C}\right)^2 + \left(\frac{\Delta H^*_{ab}}{k_H S_H}\right)^2\right]^{1/2} \tag{58.30}$$

$$S_L = 1 \tag{58.31}$$

$$S_C = 1 + 0.045C^*_{ab} \tag{58.32}$$

$$S_H = 1 + 0.015C^*_{ab} \tag{58.33}$$

The overall sensitivity factor, k_E, is used to account for variation in the illuminating and viewing conditions. A person in the textile industry who is using CMC(2:1) and would like to compare the results with CIE94 would set $k_L = 2$ and $k_C = k_H = 1$, i.e., CIE94(2:1:1).

The improvement in correlating with visual assessments of color difference could result in either the CMC(*l*:*c*) or the CIE94 replacing the CIELAB color difference equation. Hunter and Harold [30] detail many of the older color difference equations, many of which are still in use. A history of the development of color metrics was written by Richter [53].

58.8 Special Cases

Fluorescent Samples

Fluorescent materials not only reflect light but also emit light. Light absorbed at some wavelengths is emitted at longer wavelengths. The amount of light emitted depends on the intensity and the spectral power distribution of the source. Because of the emission of light, spectrophotometers that illuminate a fluorescent material with monochromatic light cannot be used, because the light emitted at the longer wavelengths will be measured as if it had been reflected from the material. Reflectance measurements of the material illuminated by polychromatic light will include the emitted light at the proper wavelengths. If the instrument's light source is a good representation of the illuminant, the measurement will be indicative of the observed color. Techniques have been recommended by the CIE for assessing the quality of daylight simulators [55]. Measured reflectance factors at the wavelengths of emittance may be greater than 1.0. Special fluorescent calibration standards must be used to accurately measure these materials [38]. The 45/0 or 0/45 bidirectional geometries are recommended for measuring fluorescent materials [39, 40].

The complete analysis of a fluorescent material requires that the emittance be separated from the reflectance. Spectrofluorimeters were designed to analyze fluorescent samples. These instruments illuminate the sample with monochromatic light. Reflected and emitted rays pass through a second monochromator to isolate the receiver wavelengths. By viewing the sample at the same wavelength as it is illuminated, the true reflectance of the sample can be determined. Either the excitance spectra or the emittance spectra can be studied by setting each monochromator at different wavelengths. Techniques have also been developed to correct spectrophotometric measurements of fluorescent samples [54, 56].

Metallic and Pearlescent Samples

Materials that contain metallic and/or pearlescent pigments are goniochromatic, i.e., they change color with the illuminating and viewing geometry. Goniospectrophotometers are needed to measure these materials. A goniospectrophotometer illuminates (or views) the sample at a fixed angle, usually 45°, and views (or illuminates) the sample at three or more angles. The position of the receivers (or illuminators) is described by the aspecular angle, the viewing angle measured from the direction of the specular reflectance, which is equal and opposite the angle of illumination. In a goniospectrophotometer that illuminates the sample at 45° and views at three angles, one of the viewing angles would be near the specular reflection at about 25°, the second at the CIE recommended bidirectional angle of 0° and the third would be far away from the specular reflectance at about 70°.

Goniospectrophotometry is still in its infancy and the CIE recommendations and ASTM standards for making these measurements are still under development.

Retroreflecting Samples

Highway signs and high visibility clothing are examples of retroreflectors. Light shining on a retroreflector is returned in directions very close to the illumination angle. Most retroreflectance measurements are made in connection with highway safety. There are only a few specially built instruments for measuring retroreflection. A projector is usually used to illuminate the sample, and a teleradiometer or a radiometric telecolorimeter is used to view the sample. Tristimulus values can be calculated from the retroreflectance factors. Standard practices and test methods exist for specifying the illuminating and viewing geometries and making retroreflectance measurements [41–45].

Lamps, Light Sources, and Displays

Spectral radiometers and radiometric colorimeters were designed to measure lamps, light sources, and displays. These instruments are similar to spectrophotometers and colorimeters but do not need an illuminator, because the sample being measured emits light.

Lamps and light sources can either be measured directly or by measuring the reflectance of a stable white reflecting surface being illuminated by the lamp or light source. To measure televisions, computer monitors, and other similar devices, the emitted light must usually be imaged directly on the optics of the spectral radiometer or radiometric colorimeter [46, 47].

Hazy and Translucent Materials

Hazy and translucent materials are measured by placing them in contact with an integrating sphere and measuring their diffuse transmittance. A haze index can be calculated from four diffuse transmittance measurements on a reflecting spectrophotometer [48]. Two of the measurements are made with a white material in the reflectance sample port, and two measurements are made with a light trap in the port. Special instruments called *hazemeters* were designed to make haze measurements.

58.9 Instrument Manufacturers

Costs of color measuring instruments vary significantly. The more accurate instruments with the best repeatability and reproducibility can be expected to cost more. Table 58.1 lists the price ranges for various types of color measuring instruments. There is a classification in the table called spectral analyzers. Although these instruments may provide information that makes them appear to be colorimeters or spectrophotometers, they use measurement techniques not traditionally associated with those instruments. For example, several use LEDs instead of more traditional light sources. Since the instruments vary so widely in capability, the purchaser must ensure that a particular instrument has the capability to make the measurements desired with sufficient accuracy, repeatability, and reproducibility.

TABLE 58.1 Color Measuring Instruments and Their Costs

Instrument type	Price range in US $
Colorimeters	4,000–15,000
Goniospectrophotometers	12,500–30,000
Hazemeters	13,000–15,000
Radiometric Colorimeters	2,000–10,000
Retroreflectometers	3,500–15,000
Spectral Analyzers	1,500–2,500
Spectrofluorimeters	30,000–40,000
Spectrophotometers	2,500–20,000
Spectroradiometers	2,500–40,000

Table 58.2 provides contact information for a number of manufacturers of color measuring instruments. The manufacturers listed in this table design instruments specifically for color measurement. Thus, manufacturers of analytical spectrophotometers are excluded even if their instruments have color measuring capabilities. The table is also limited to manufacturers with a major presence in the U.S.

TABLE 58.2 Instrument Manufacturers

BYK-Gardner USA Rivers Park II, 9104 Guilford Road Columbia, MD 21046-2729 (301) 483-6500 Spectrophotometers, colorimeters, hazemeters	**Color Savvy, Ltd.** 305 S. Main Street Springboro, OH 45066 (513) 748-9160 Colorimeters, spectrophotometers
ColorTec 28 Center Street Clinton, NJ 08809 (908) 735-2248 Spectral analyzers	**Datacolor International** 5 Princess Road Lawrenceville, NJ 08648 (609) 924-2189 Spectrophotometers, goniospectrophotometers
Datacolor International 5 Princess Road Lawrenceville, NJ 08648 (609) 924-2189 Spectrophotometers, goniospectrophotometers	**Gamma Scientific Co.** 8581 Aero Drive San Diego, CA 92123 (619) 279-8034 Spectroradiometers, retroreflectometers
GretagMacbeth 617 Little Britain Road New Windsor, NY 12553-6148 (914) 565-7660 Spectrophotometers, goniospectrophotometers	**Hunter Associates Laboratory, Inc.** 11491 Sunset Hills Road Reston, VA 20190 (703) 471-6870 Spectrophotometers, colorimeters
Labsphere, Inc. P.O. Box 70, Shaker Street North Sutton, NH 03260-0070 (603) 927-4266 Spectroradiometers, radiometric colorimeters, spectrofluorimeters	**Light Source, Inc.** 4th floor, 4040 Civic Center Drive San Rafael, CA 94903 (415) 446-4200 Spectrophotometers, spectroradiometers
Minolta Corporation 101 Williams Drive Ramsey, NJ 07446 (201) 825-4000 Spectrophotometers, spectroradiometers, colorimeters, radiometric colorimeters, spectrofluorimeters	**Photo Research Inc.** 9330 DeSoto Avenue Chatsworth, CA 91311 (818) 341-5151 Spectroradiometers
X-Rite, Inc. 3100 44th St. SW Grandville, MI 49418 (616) 534-7663 Spectrophotometers, spectrocolorimeters, goniospectrophotometers	

58.10 Defining Terms

For a more extensive collection of terms relating to color and appearance, the reader should refer to ASTM E 284 Standard Terminology of Appearance [49].

Chroma: Attribute of color used to indicate the degree of departure of the color from a gray of the same lightness.

CIE: The abbreviation for the French title of the International Commission on Illumination, Commission Internationale de l'Éclairage.

CIE standard observers: The ideal colorimetric observer data adopted by the CIE to represent the response of the average human eye, when light-adapted, to an equal-energy spectrum. The standard observer adopted in 1931 was developed from data obtained with a 2° field of vision and is commonly called the "2° standard observer." The standard observer adopted in 1964 was developed from data obtained with a 10° annular field of vision and is commonly called the "10° standard observer."

CIE tristimulus values: Amounts of the three mathematical lights necessary in a three-color additive mixture required for matching a color in the CIE System. They are designated *X*, *Y*, and *Z*. The illuminant and standard observer color matching functions must be designated.

colorimetry: The science of color measurement.

hue: The attribute of color perception by means of which a color is judged to be red, orange, yellow, green, blue, purple, or intermediate between adjacent pairs of these, considered in a close ring (red and purple being an adjacent pair.) White, black and grays possess no hue.

illuminant: A mathematical description of the relative power emitted by a real or imaginary light source at each wavelength in its emission spectrum.

lightness: (1) The attribute of color perception by which a nonself-luminous body is judged to reflect more or less light. (2) The attribute by which a perceived color is judged to be equivalent to one of a series of grays ranging from black to white.

metamerism: Property of two specimens that match under a specified illuminator and to a specified observer and whose spectral reflectances or transmittances differ in the visible wavelengths.

perfect reflecting diffuser: Ideal reflecting surface that neither absorbs nor transmits light, but reflects diffusely, with the radiance of the reflecting surface being the same for all reflecting angles, regardless of the angular distribution of the incident light.

reflectance: Ratio of the reflected radiant or luminous flux to the incident flux in the given conditions. The term reflectance is often used in a general sense or as an abbreviation for reflectance factor. Such usage may be assumed unless the above definition is specifically required by the context.

reflectance factor: Ratio of the flux reflected from the specimen to the flux reflected from the perfect reflecting diffuser under the same geometric and spectral conditions of measurement.

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