Colour Science

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These notes were originally produced as part of the study materials for SEF 211 *Colour Science and Colouration Technology*, which was one of the units offered by the School of Engineering and Technology in Deakin University's flexible learning program.

First published by:
Deakin University,
Geelong,
Victoria 3217,
Australia

Contents

Colour science

Overview of the unit

This course provides a comprehensive introduction to colour science. It deals with the nature and origins of colour, its measurement and the uses of colour measurement in the textile industry. It is intended to be a basis for future work and study in specialist areas concerned with textiles, as well as providing an overview for management purposes.

Our whole lives are bathed in colour, there is colour in the daylight, in the sky, in the landscape, in our skin, hair and eyes. Every object we manufacture to use or wear is coloured. Colour can influence our moods and perceptions making things warm or cold, provocative or sympathetic, exciting or tranquil. Colour provides us with information. We stop at red lights and move on when they change to green. We avoid eating unripe fruit and vegetables. Colour is a major factor in our decisions about which textiles to buy and has enormous economic significance. Study of the science of colour helps us to measure it, reproduce it, and manufacture coloured substances which can be applied to almost any article using appropriate technology.

Every modern dyehouse of reasonable size has a colour kitchen in which colour matching and recipe prediction are carried out using specialised measuring equipment and computer software. This equipment saves a significant amount of time and money in making it possible for trained experts to produce desired colours on textiles more accurately than can be done without colour measurement equipment.

These notes are intended to lay out the basis for understanding the theory of colour perception and measurement and to show how colour measurement is used in the textile industry to match colours and predict colours from basic measured information.

Topic 1.

Measurement of colour

Introduction

The measurement of colour started with Lovibond, a Brewer in England, who wanted to produce beer with a consistent colour. However, it has only been possible to measure colour in a universal sense within the last seventy years. The basic principles were agreed on a worldwide basis in 1931. However, the most notable advances have had to await the development solid-state electronics and computers before sufficient processing power was available to simulate processes occurring in our brain which we take more or less for granted.

Objectives

At the end of this topic you should be able to:

- *define colour,*
- *describe how colour is perceived by the human eye,*
- *have a general appreciation of how colour is related to chemical constitution,*
- *understand the CIE tristimulus colour measurement system and how it relates to human colour perception.*

What is colour?

According to the Committee on Colourimetry of the Optical Society of America, colour is defined as consisting of the characteristics of light other than spatial and temporal inhomogeneities. Furthermore, light is described as the aspect of radiant energy which is apparent to a human observer through the visual sensations which arise from the stimulation of the cone and rods cells in the retina of the eye. Stimulation of the receptor cells initiates nerve impulses that are translated in the brain into a visual sensation of color. Therefore, colour defined in this way is a psychological response to a physical stimulus produced by means of a physiological process.

The chain of events involved in the perception of colour is illustrated in Figure 1.1. Light emitted from a source illuminates an object, the object reflects and scatters the light which falls on it, some of the light enters the eye and the detector cells produce electrical signals which are interpreted by the brain.

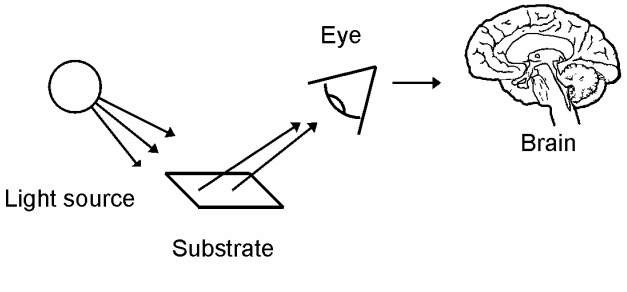

Figure 1.1 The process of vision

Not only colour information is sent by the eye to the brain. Spatial variations in colour are interpreted by the brain to provide a camera-like perception of everything we see. The brain is not a perfect machine, it is capable of producing false perceptions of the physical world and not all brains operate in quite the same way. Colour illusions occur (which are analogous to optical illusions) and about 10% of people have various forms of colour blindness which mean that they perceive colour differently from the majority. Therefore, it is accepted that no instrument can measure perceived colour accurately in all situations for all people. However, the physical properties of light sources, substrate reflectance and light sensitivity of the eye can all be measured accurately and these physical quantities can be correlated with perceived colour in a way which is meaningful to the majority of people in many situations.

The human eye

The basic structures of the eye are shown in Figure 1.2.

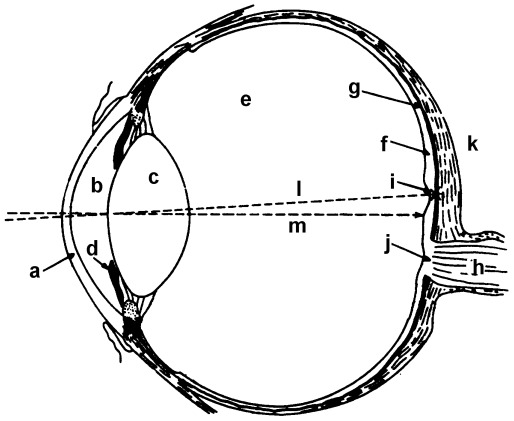

Figure 1.2 The human eye, (a) cornea, (b) aqueous humor, (c) lens, (d) iris (e) vitreous humor, (f) retina, (g) choroid (pigmented membrane), (h) optic nerve, (i) fovea, (j) optic disc (blind spot), (k) sclera, (l) visual axis, (m) optical axis.

The light entering the eye through the cornea is controlled by the iris and focussed on the retina by the combined action of the cornea and the lens. The images received by the eye are inverted compared with the real world. In

camera terms the effective aperture range of the pupil in the iris is from f2.5 to f13. The aqueous and vitreous humor are clear viscous liquids. The retina is the light sensitive structure. It is about 0.1 mm thick and lines the back surface of the eye. The outermost layer of the retina (i.e. the layer closest to the outside of the eye) contains the photosensitive receptors known as rods and cones. The light sensitivity of rods and cones is very different. Rods are almost 1000 times more sensitive than cones and are responsible for vision at low levels of illumination (e.g. starlight which corresponds to less than 1 lux). Rods only register levels of lightness and darkness, so we are unable to see colours. This is called scotopic vision. At higher light levels, cones provide us with colour vision and the ability to see fine detail. This is called photopic vision.

The rods and cones vary in their density distribution around the retina. Only cones are present at the point where the primary visual axis of the eye intersects the retina, and here they occur at their maximum density. This is a small approximately circular area subtending about 1^o in diameter called the foveola. It corresponds to the point of maximum resolution in the retina where it is possible to resolve detail of the order of 1/60th of a degree). This resolving power fails off rapidly with increasing distance from the foveola. A large proportion of the cone cells are contained within the fovea which occupies about a 5^o field of view. Almost all the cones are contained within the macula which occupies a 20^o field. An illustration of how the rods and cones are distributed around the foveola is shown in Figure 1.3.

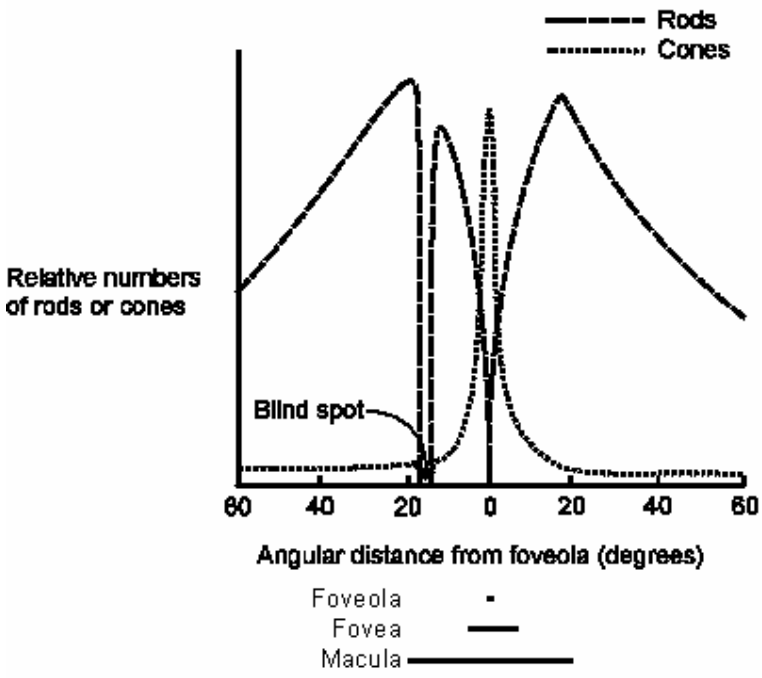

Figure 1.3 An illustration of how the rod and cone cells are distributed in the retina

Figure 1.4 is a simplified schematic diagram of a transverse section through the retina. The rods and cones are and overlaying these is a complex arrangement

of specialized nerve cells and nerves.

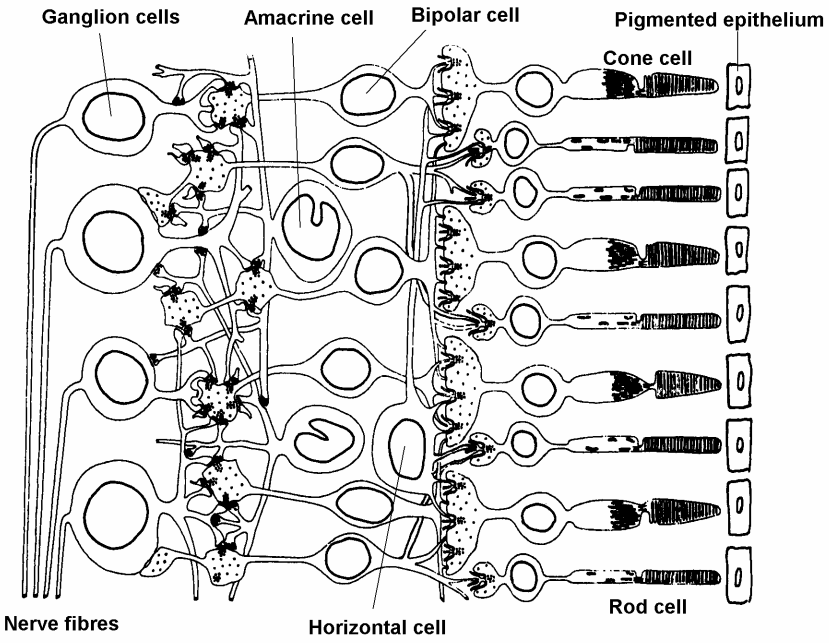

Figure 1.4 A simplified diagram of a section through the retina. Note that light travels from left to right i.e. the nerve cells and fibres overlay the rod and cone cells

The photosensitive pigments are contained within the outer segments of the rods and cones. There are four different photo-pigments one contained within the rods and three different types distributed amongst the population of cones. The visual pigment found in the rods is known as rhodopsin. It absorbs light mostly in the yellow part of the spectrum (at a wavelength of about 496 nm) and transmits light at both the violet and red ends of the spectrum. The peak sensitivities of the cones lie in the blue (approx. 425 nm), green (approx. 530 nm) and yellow-green (approx. 560 nm) parts of the spectrum. The visual pigments are all closely related to rhodopsin. The three different types of cone cells do not occur with equal frequency throughout the retina. There are approximately 40 red and 20 green to every blue sensitive cell, and in the foveola, the blue cones are almost entirely absent. The probability of absorbance of a quantum of light therefore varies not only according to wavelength but also on the relative distribution of cone types.

Carrots, alkenes, and the chemistry of vision

Folk medicine has long held that eating carrots is good for your eyes. Although that's probably not true for healthy adults on a proper diet, there is no question that the chemistry of carrots and the chemistry of vision are related. Carrots are rich in β-carotene, a purple-orange alkene that is an excellent dietary source of vitamin A. β-Carotene is converted to vitamin A by enzymes in the liver, oxidized to an aldehyde called 11-*trans*-retinal, and then isomerised by a

change in geometry of the C11-C12 double bond to produce 11-*cis*-retinal, the light-sensitive pigment on which the visual systems of all living things are based (See Figure 1.5).

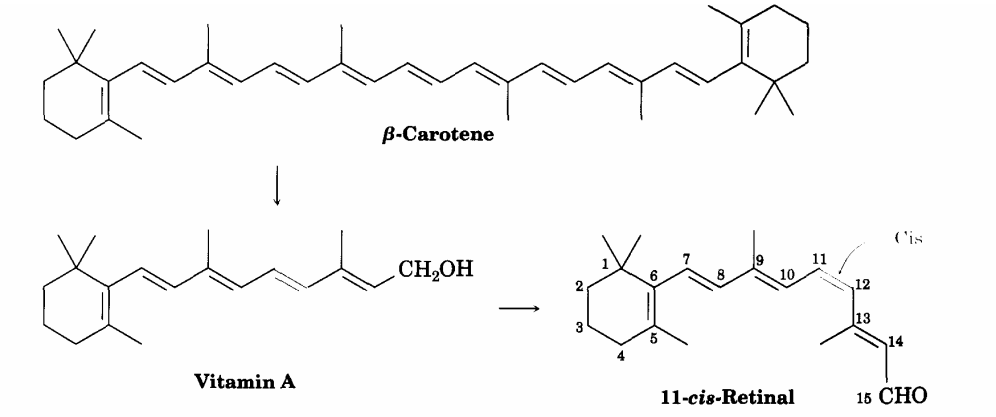

Figure 1.5 Conversion of *β*-carotine to 11-*cis*-retinal

In the rod cells of the eye, 11-*cis*-retinal is converted into rhodopsin, a light-sensitive substance formed from the protein opsin and 11-*cis*-retinal. When light strikes the rod cells, isomerisation of the C11-C12 double bond occurs and *trans*-rhodopsin, also called *meta*-rhodopsin II, is produced. This cis-trans isomerisation of rhodopsin is accompanied by a change in molecular geometry (shown in Figure 1.6), which in turn causes a nerve impulse to be sent to the brain where it is perceived as vision. (In the absence of light, the cis-trans isomerisation takes approximately 1100 years; in the presence of light, it occurs within 2 x 10^{-11} seconds!)

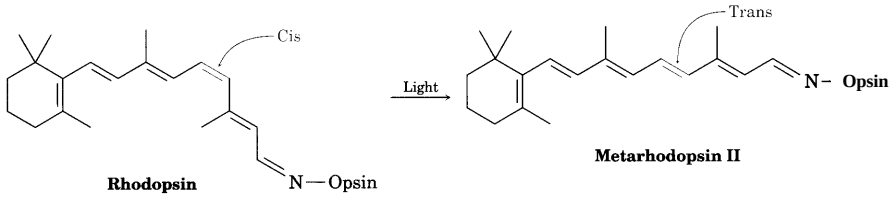

Figure 1.6 The effect of light on rhodopsin

Ops

Meta-rhodopsin II is then recycled back into rhodopsin by a multi-step sequence involving cleavage to 11-*trans*-retinal and cis-trans isomerisation back to 11-*cis*-retinal.

When a visual pigment molecule absorbs a quantum if light and fires to produce the small electrical signal, its colour also lightens. This is called photo-bleaching. In fact, a flash of light is not actually perceived unless nine adjacent cells fire together and then only with 60% probability. Photo-pigments return to their original receptive *cis* state within several seconds and under a moderate level of light stimulation, a steady state exists in which the

rates bleaching and regeneration are equal. In very bright light much of the visual pigment becomes bleached and the sensitivity of the eye to colour is much reduced. Also at high levels of illumination, we loose sensitivity to the violet and red colours at opposite ends of the spectrum and our vision tends towards a bicolour system sensitive to only yellow and blue. Whereas, when the eye becomes adapted to very dark conditions its sensitivity reaches a maximum. However because the rods are much more sensitive than cones, colour vision is lost and detail is seen only in the peripheral visual region outside the macular disk of the retina. It is obvious from the foregoing that:

- the solid angle of the light entering the eye will have a considerable influence on colour vision and has to be taken into account when choosing conditions for viewing and measuring coloured samples
- when viewing colours for comparison purposes, the lighting should be not too bright or dark for photopic vision to be optimal and approximately 1500 lux is an appropriate lighting level.

The existence of three types of colour receptors (red, green and blue) in the eye was suggested as long ago as 1801 by Young in his theory of visual trivariance. This was later further developed by Helmholtz and is now known as the Young-Helmholtz theory of trichromatic vision. However, in 1878 Hering suggested that visual perception is based on six different receptors for the colours - red, green, yellow, blue, white and black. These receptors were arranged into three pairs. All colours could then be described in terms of their levels of stimulation of pairs of red - green, yellow - blue and white-black receptors and this was called the opponent theory or the theory of the three antagonistic or opposed pairs of receptors. In 1930 Muller pointed out that both theories were compatible. He confirmed that there were three types of colour receptor cells in the eye but the electrical signals from these cells were converted by interconnected nerves in the retina into three pairs of antagonistic signals which were sent to the brain as red - green, yellow - blue and white-black responses. The opponent theory of colour vision is illustrated in Figure 1.7. Experiments involving direct measurements of electrical signals in the optic nerves of primates have subsequently shown that the three types of responses do occur.

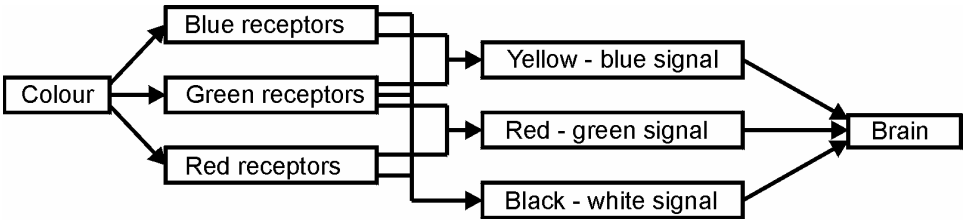

Figure 1.7 The opponent theory of colour vision

The physical basis for colour

Colour of objects originates from absorption of visible light by electrons when they are promoted from lower to higher energy states within molecules. As far

as organic molecules such as dyes are concerned, suitable energy states for electronic transitions are generally only found in molecules with extended conjugated double bond systems. The structures of these molecules will be discussed in the module on Colouration technology. The electronic transitions in dyes usually involve promotion of electrons from non-bonding and π-bonding orbitals to antibonding π* orbitals, as a result of absorption of a quantum of energy. The energy associated with a transition in quantum electronic states (ΔE) is related to the wavelength of the radiation as given by Planck's Law:

$$\Delta E = h\nu$$

where h is Planck's constant = 6.626176×10^{-34} J s, and ν is the frequency of the radiation which is related to its wavelength (λ) by the relationship $c = \nu\lambda$, where c is the velocity of light = 2.997925×10^{8} m s^{-1}.

How colour is perceived

Read Sections 4.1 and 4.2 in The Dyeing of Textile Fibres by J Rivlin, Philadelphia College of Textiles and Science, Pennsylvania, USA (1992) (the textbook for the module on Colouration technology) for information on the three ways in which colours can be generated:

- by visible electromagnetic radiation of a single wavelength,
- by an additive process which involves mixing of coloured lights,
- by a subtractive process in which coloured substances are mixed together. This is the process involved in colouring textiles.

Note that mixing colours by an additive process produces a resultant colour which tends to white, while subtractive mixing always darkens perceived colour and tends towards black.

Also note the anecdotal evidence presented on how illumination from different types of sources can effect the perceived colour of materials coloured by additive processes.

Tristimulus values

The International Committee on Illumination (Commission Internationale de L'Eclairage or CIE), which is accepted worldwide as the body which sets definitions and standards for the specification of colours, has formulated a system which measures colour numerically in terms of 'tristimulus values' X, Y, Z. The theory is based on the fact that the human eye appears to function as though it has three types of receptor cells which absorb light in different regions of the visible spectrum: one for blue-violet, one for green and one for red which has also some blue-violet absorption. The spectral sensitivities of the three receptors have been defined by the CIE for a standard observer.

The tristimulus values of a sample therefore represent the amounts of red (X), green (Y) and blue (Z) primary colours respectively, which are necessary to produce the 'colour' of that sample.

The tristimulus values (X, Y and Z) of a sample are determined from three quantities already identified as being involved in the perception of colour. These are:

- the spectral radiant flux incident on the object per unit area for a given source of light - E_λ,
- the tristimulus eye sensitivity functions of the CIE standard observer, $\bar{x}_\lambda$, $\bar{y}_\lambda$ and $\bar{z}_\lambda$
- the reflectance from the sample, R_λ.

The definition of the tristimulus values is as follows:

$$X = k \int_{\text{Min}\,\lambda}^{\text{Max}\,\lambda} E_\lambda \, \bar{x}_\lambda \, R_\lambda \, d\lambda$$

$$Y = k \int_{\text{Min}\,\lambda}^{\text{Max}\,\lambda} E_\lambda \, \bar{y}_\lambda \, R_\lambda \, d\lambda$$

$$Z = k \int_{\text{Min}\,\lambda}^{\text{Max}\,\lambda} E_\lambda \, \bar{z}_\lambda \, R_\lambda \, d\lambda$$

where:

$$k = \frac{100}{\int_{\text{Min}\,\lambda}^{\text{Max}\,\lambda} E_\lambda \, \bar{y}_\lambda \, d\lambda}$$

Here λ, denotes the wavelength of the radiation in nm (nanometer). The integration is usually performed over a wavelength range of 380-740 nm which is approximately the wavelength visible to the human eye. The reflectance readings are generally obtained using a colorimeter or spectrophotometer, using a diffuse reflectance measurement system. The constant k is used to ‘normalize’ the results.

Illuminants

The standard illuminants defined by the CIE in 1971 are as follows:

- Illuminant A. This corresponds to a gas-filled incandescent lamp operated at a correlated colour temperature of 2854°K.
- Illuminant B. (Noon sunlight). This corresponds to the same lamp as in Illuminant A in combination with a two-cell Davis-Gibson liquid filter giving a correlated colour temperature of 4870°K.
- Illuminant C. (Average daylight). This corresponds to an incandescent source with a correlated colour temperature of 6770°K.

- Illuminant $D_{65,}$. This corresponds to an illuminant having a correlated colour temperature 6500°K. It is similar to Illuminant C but includes an ultraviolet component and is closer to natural daylight at lower latitudes.

The energy spectra of the standard illuminants are shown in Figure 1.8. Detailed data are listed in standard tables.

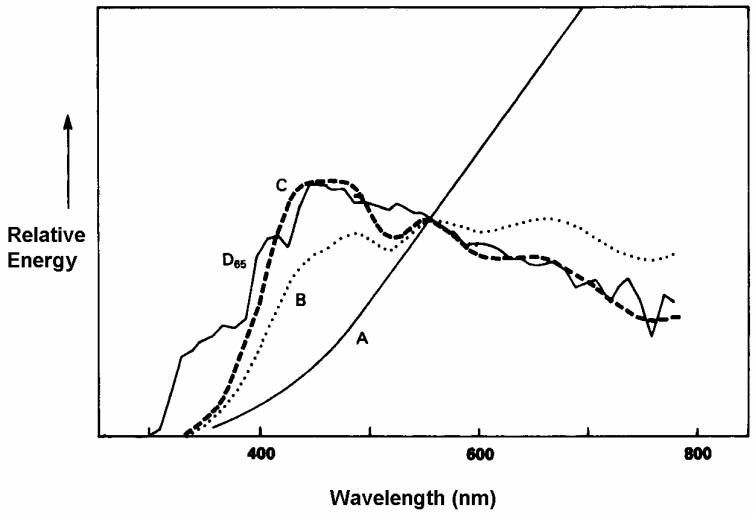

Figure 1.8 The spectra of standard CIE Illuminants

It is obvious that the illuminant should always be specified whenever tristimulus values are quoted.

Black body radiators

An illuminant may or may not exist physically. The energy output from incandescent black body radiators may approximate to some of the standard illuminants, such as illuminants A and C. In some cases filters are used to modify the energy distribution from incandescent radiators to approximate the defined energy distributions (e.g. Illuminant B).

The continuous spectrum of radiation emitted by a black body (perfect radiator) is described by Planck's radiation law. The spectral emittance of a black body (M_λ) is given by :

$$M_\lambda = \frac{2\pi hc^2 \times 10^{-9}}{\lambda^5\left[\exp(hc/\lambda kT) - 1\right]}$$

where λ is the wavelength, h is Planck's constant, c is the velocity of light, K is Boltzmann's constant and T is the absolute temperature in ^oK.

Thus, the spectrum of the spectral energy distribution is determined only by the absolute temperature of the source. Black body radiators are characterised by

very wide energy distributions, as shown in Figure 1.9. Black bodies with temperatures around 6000^{o}K have emission maxima in the visible region but emit strongly in both the ultraviolet and infrared. The emission peak shifts to longer wavelengths as the temperature decreases.

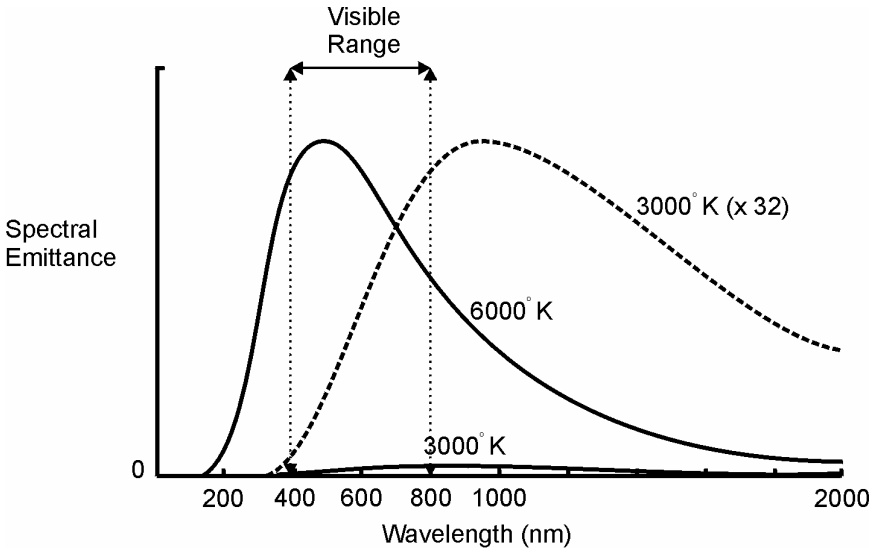

Figure 1.9 The spectral energy distributions of black body radiators

Incandescent lamps nearly behave as black body radiators and the temperatures of their filaments can be regulated to colour temperatures between 2800^{o}K and 3400^{o}K. The sun approximates a black body radiator of 6565^{o}K outside the earth's atmosphere but at the surface is vary variable depending on the time of day and atmospheric conditions. The jagged appearance of the energy distributions of the Illuminants is due to selective absorption and scattering of certain wavelengths by constituents of the earth's atmosphere. Illuminants B, C and D_{65} are intended to simulate sunlight under different conditions, whereas illuminant A represents artificial light from an incandescent source. You can see how close the CIE standard illuminants are to black body radiators by comparing the curves in Figures 1.8 and 1.9. The correlated colour temperature of a source is the temperature of the black body radiator which gives a similar wavelength distribution of spectral emittance.

Fluorescent and arc sources

Some sources have energy distributions very different from black body radiators and consist of spectral lines rather than distributions. The most commonly encountered are gas discharge tubes (Figure 1.10) and fluorescent lamps (Figure 1.11). Colours viewed under these sources of illumination can appear very different from the colours seen under standard illuminants, as already noted above. Tristimulus values can be computed with these sources, even though they are not standard illuminants.

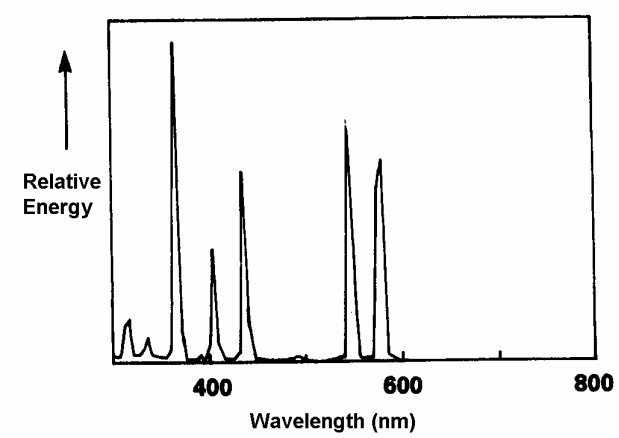

Figure 1.10 The spectral energy distribution of a high pressure mercury lamp

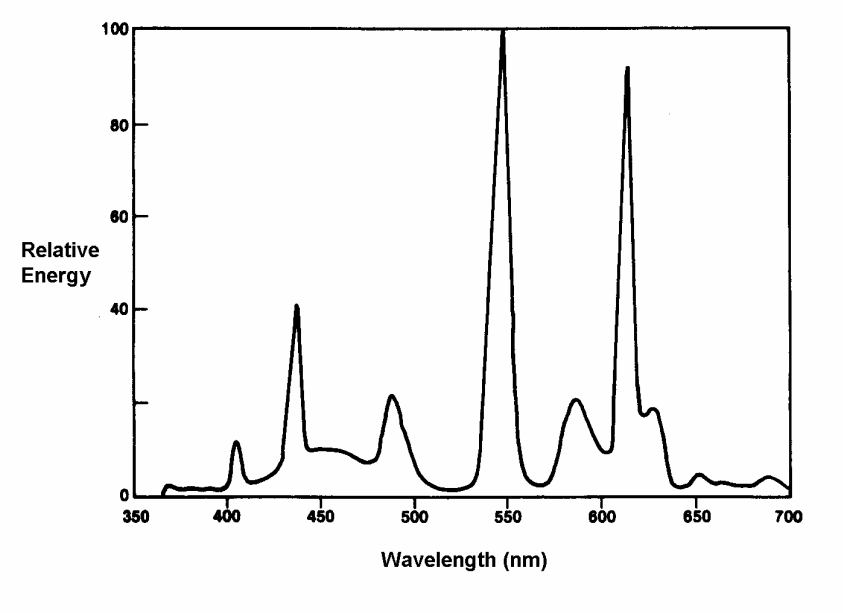

Figure 1.11 The spectral energy distribution of a fluorescent lamp (TL84)

Light from an arc lamp, such as a high-pressure xenon arc lamp, contains emission lines against a background of black body radiation and when this source is combined with suitable filters, reasonable approximations can be obtained to Illuminant D_{65} as shown in Figure 1.12.

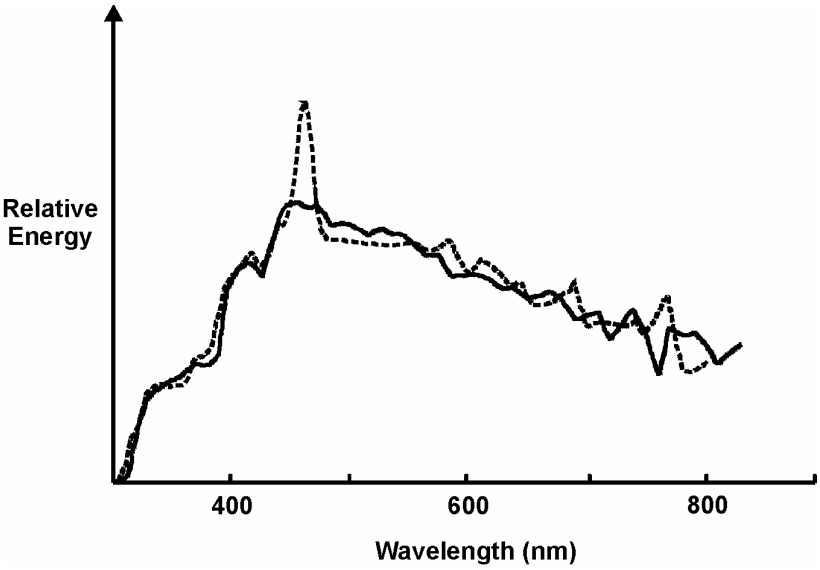

Figure 1.12 The spectral energy distribution of a filtered high-pressure xenon arc lamp (dotted curve) compared with Illuminant D_{65} (solid curve)

Light from high-intensity, high-pressure xenon arc lamps is commonly used in modern reflectance spectrometers to illuminate samples during measurement.

The CIE tristimulus eye sensitivity functions

As already described, it was found that the wavelength sensitivity of the receptor cells in the retina of the eye varied with the solid angle of the cone of light entering the eye. Originally in 1931, data was compiled for a standard 2^o observer and in 1964 data for a 10^o observer was published and this is normally preferred today because it is more accurate for use with samples viewed close to the eyes. The CIE-defined sensitivity functions for the receptors are illustrated in Figure 1.13. Detailed data are listed in standard references. In fact, these functions do not exactly follow the sensitivities of the visual pigment in the eyes, nor do they need to. It turns out from tristimulus theory that many combinations of three theoretical functions can be used. The CIE recommendation provides that all realisable colours can be synthesised using positive contributions of the functions.

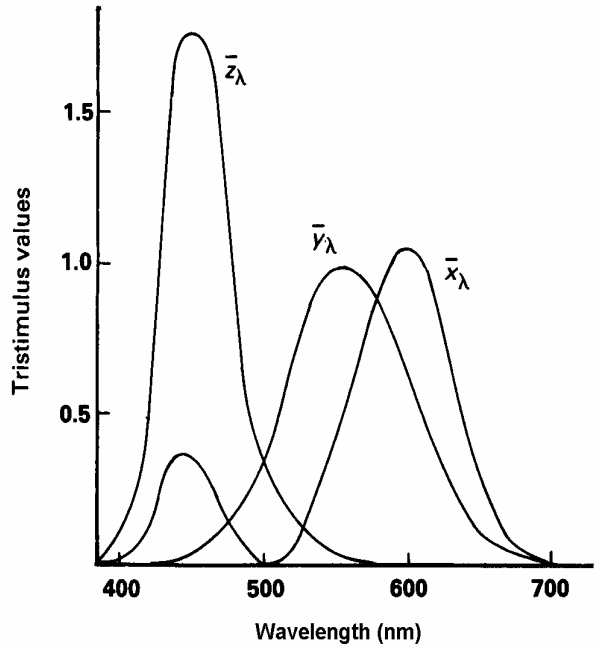

Figure 1.13 Tristimulus eye sensitivity functions for the 10^o observer.

Calculation of tristimulus values

In practice, tristimulus values are calculated by summing the product of reflectance values at particular wavelengths (R_λ) with values of $E_\lambda\, x_\lambda$, $E_\lambda\, y_\lambda$ and $E_\lambda\, z_\lambda$. Appropriate values are calculated from CIE data which is given at 5 nm intervals. Many spectrophotometers give reflectance readings at 20 nm intervals from 400 nm to 700 nm. For this experimental situation, the data calculated by the method of Stearnes for 20 nm intervals are given in Table 1.1 for illuminants A and D_{65} and source TL84.

Table 1.1 Adjusted values of $E_\lambda\bar{x}_\lambda$, $E_\lambda\bar{y}_\lambda$ and $E_\lambda\bar{z}_\lambda$ of various illuminants and sources for the CIE 1964 (10^o) standard observer

λ (nm)	$\mathbf{E_\lambda\bar{x}_\lambda}$	$\mathbf{E_\lambda\bar{y}_\lambda}$	$\mathbf{E_\lambda\bar{z}_\lambda}$
Illuminant A			
400	0.0341	0.0028	0.1393
420	0.7924	0.0807	3.7800
440	1.8956	0.3049	9.7345
460	1.9781	0.8593	11.5226
480	0.7178	2.1351	6.7697
500	0.0368	4.8855	2.2987
520	1.5225	9.6529	0.7469
540	5.6742	14.4638	0.2005
560	12.4369	17.4842	0.0051
580	20.5461	17.5799	- 0.0020
600	25.3716	14.9062	0.0000
620	21.5928	10.0811	0.0000
640	12.1586	5.0618	0.0000
660	4.6354	1.8191	0.0000
680	1.3936	0.5401	0.0000
700	0.3755	0.1426	0.0000
Total	111.1620	100.0000	35.1953
lIluminant D_{65}			
400	0.2516	0.0236	1.0906
420	3.2317	0.3301	15.3824
440	6.6805	1.1069	34.3830
460	6.0964	2.6206	35.3562
480	1.7213	4.9378	15.8979
500	0.0589	8.6695	3.9972
520	2.1845	13.8473	1.0457
540	6.8093	17.3537	0.2373
560	12.1626	17.1539	0.0025
580	16.4686	14.1481	-0.0022
600	17.2340	10.1056	0.0000
620	12.8953	6.0212	0.0000
640	6.2267	2.5867	0.0000
660	2.1113	0.8268	0.0000
680	0.5736	0.2222	0.0000
700	0. 1209	0.0460	0.0000
Total	94.8272	100.0000	107.3906
Source TL84			
400	-0.0461	-0.0112	-0.2963
420	1.5506	0.1834	7.5982
440	6.0062	0.9472	30.6828
460	2.5775	0.9644	14.8026
480	0.8133	3.6086	8.5908
500	0.0316	3.2778	2.7320
520	-0.6801	-0.6157	-0.1727
540	17.7978	39.4158	0.3538
560	8.5749	16.7056	0.0901
580	9.7913	6.9700	-0.0134
600	22.2285	12.7295	0.0000
620	31.3897	14.9826	0.0000
640	1.9177	0.7193	0.0000
660	0.2442	0.0814	0.0000
680	0.0810	0.0312	0.0000
700	0.0258	0.0101	0.0000
Total	102.3039	100.0000	64.3679

Review questions

1. *What part of the visible light is absorbed when the color of the object seen at day light is:*
2. *a. magenta b. red c. brown d. grey e. cyan*
3. *By mixing yellow, cyan, and magenta paints, how would you make:*
4. *a. blue b. red c. olive d. navy blue c. brown grey*
5. *A red light, a green light, and a blue light, are alternately projected at the same spot on a white screen. What color will appear on the screen when:*
    a. *the red light and the blue light are projected simultaneously?*
    b. *b. the green light and the red light are projected simultaneously?*
    c. *c. the blue light and the green light are projected simultaneously?*
6. *What color would a blue car appear to be under an all-yellow sodium vapor street light? ExplainRivlin (1992), page 203, Colour and Chemical constitution, questions 2 - 5.*
7. *What is the difference between scotopic and photopic vision?*
8. *What are the most important factors to be considered when viewing samples for colour assessment?*
9. *What is the difference between the trichromatic and opponent theories of colour vision?*
10. *What is the difference between an illuminant and a source?*
11. *Contrast the spectral energy distributions of illuminants D_{65} and A.*
12. *How are tristimulus values related to theories of colour vision?*

Topic 2.

Measurement of reflectance spectra

Introduction

In this topic you will learn about unique properties of reflecting surfaces and how these are taken into account when reflectance is measured. Instruments for accurate measurement of reflectance will be briefly described.

Objectives

At the end of this topic you should be able to:

- *explain how reflectance is related to colour,*
- *understand the relationship between scattering, and absorption of light in a textile substrate in terms of The Beer-Lambert law and the Kubelka-Munk equation,*
- *describe the operating principles of colourimeters and a spectrophotometers*
- *understand how reflectance measuring instruments are calibrated and samples presented,*
- *appreciate the different requirements for measurement of fluorescent samples.*

Basic principles

Reflectance spectra may be measured by instruments which record reflectance continuously across the visible spectrum. Spectrophotometers for use on the colouration industry produce reflectance readings in the visual colour range of 380 nm to 740 nm. Block diagrams of this type of machine are shown in Figure 2.1.

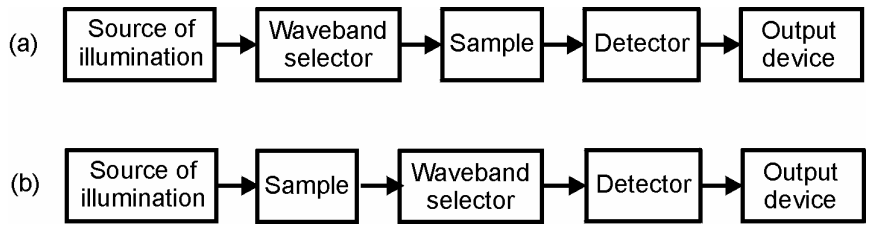

Figure 2.1 The basic elements of a spectrophotometer, (a) monochromatic illumination, (b) full spectrum illumination

Note that in some spectrophotometers the samples are illuminated with monochromatic light and in others directly by the source. The type of waveband selector used varies considerably. The earliest instruments used prism or grating monochromators to disperse light to a resolution of less than 1nm and also used a single detector. This type of spectrometer was suitable for scientific purposes but usually took several minutes to complete a scan. This

was too slow to make the machine suitable for routine industrial measurements. Faster measurements became possible by the use of narrow-band interference filters instead of monochromators. Narrow-band interference filters typically pass a band of radiation 20 nm wide so the spectrum consisted of a histogram of reflectance measurements. Approximately 16 filters were mounted on a wheel which was rotated to bring the filters sequentially into the optical path in the instrument. However, modern reflectance spectrophotometers use gratings and solid-state array detectors so that measurements can be made simultaneously across the whole visible spectrum. The resolution bandwidth of spectrophotometers, with solid state array detectors is typically between 5 and 20 nm. Plotted spectra from filter and solid state detector machines are usually smoothed to give continuous curves.

Relationship between reflectance and colour

Typical reflectance spectra are shown in Figure 2.2.

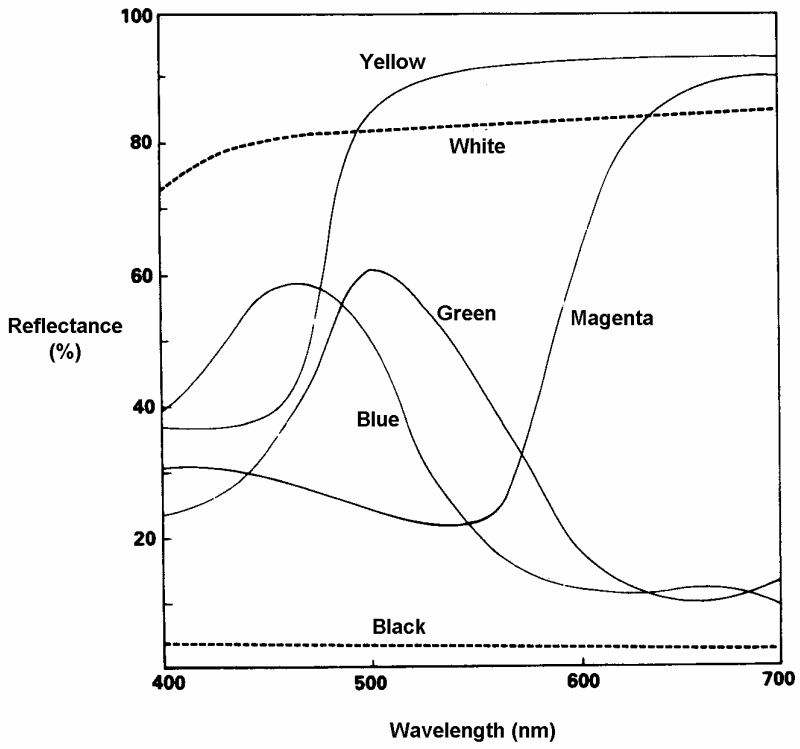

Figure 2.2 Typical reflectance spectra of different coloured samples

Note that the shape of the measured spectrum is determined by the absorption of light of different wavelengths by colour absorbing chromophores within the sample. In other words, the reflection spectrum consists of light not absorbed by the sample. The light absorbed by certain colours is illustrated in Table 2.1.

Table 2.1 The relationship between reflected colour and absorbed colour in a sample

Colour of reflected light from a substrate	Colour of light absorbed
Magenta	Green, violet, some blue
Green	Red, blue, violet
Yellow	Violet-blue
Blue	Yellow-green, yellow, orange and some red

Scattering and absorption by a textile substrate

When light is incident on the surface of the specimen, the part that is reflected at an angle equal to the angle of incidence (mirror image reflection) is called the specular reflection or specular component and the part that is reflected at all other angles is called the diffuse reflection or diffuse component. This is illustrated in Figure 2.3.

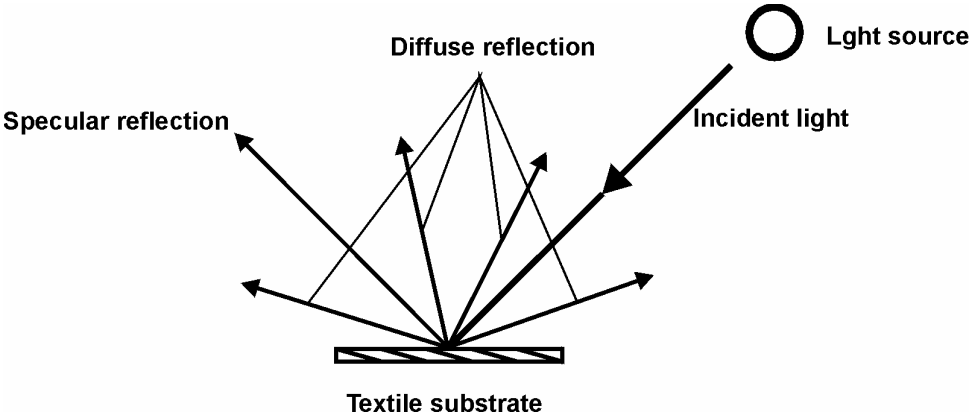

Figure 2.3 The specular and diffuse components of reflectance

The more glossy the surface, the greater the contribution to the specular component. For a matte surface the specular component is very low.

Textile samples are usually composed of fibres arranged in different ways so to examine the causes of reflection and absorption in textiles it is appropriate to consider single fibres in the first instance.

Interaction of a light beam with a single fibre

If we consider a ray of monochromatic light striking the surface of a fibre at an angle *i* to the normal, then a proportion (*R*) of the light will be reflected and this is given by Fresnel's formula:

$$R = \frac{1}{2}\left[\frac{\sin^2(i-r)}{\sin^2(i+r)} + \frac{\tan^2(i-r)}{\tan^2(i+r)}\right]$$

where $\frac{n_1}{n_2} = \frac{\sin r}{\sin i}$ and n_1 is the refractive index of air (nearly equal to unity), n_2 is the refractive index of the fibre (the refractive index of wool is 1.3) and r is the angle to the normal of the refracted ray within the fibre. This is illustrated in Figure 2.4.

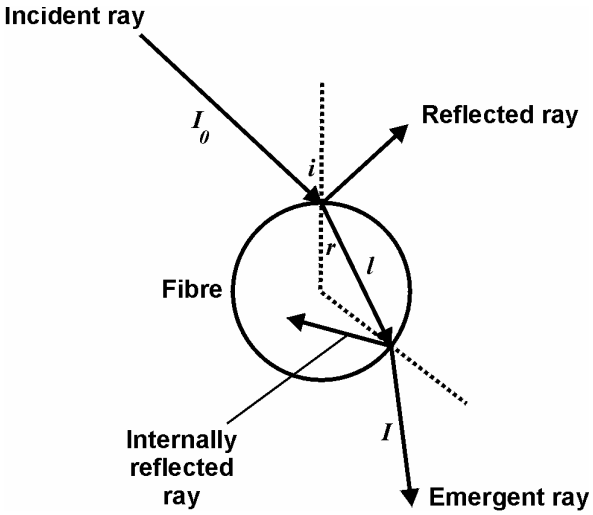

Figure 2.4 Reflection and transmission of a light ray striking a fibre

Thus if a ray of monochromatic light strikes a wool fibre (n = 1.3) at an angle of incidence of 45^o, 2.4% of the light will be reflected and the beam will pass into the fibre at 33^o.

The beam traversing the fibre may be absorbed to some extent if chromophores are present and the absorption process will be described by the Beer-Lambert law. When the beam has traversed the fibre, a small proportion of the remaining energy will be internally reflected (a few percent, determined by the angle at which the beam strikes the surface) and the remaining radiation will pass out of the fibre at an angle determined by Fresnel's formula.

The Beer-Lambert law

Dyes inside fibres usually behave as though they are dissolved in the fibre and their absorption behaviour is similar to that of solutions. The absorption of light in dyed fibres is governed by two laws. The first is Lambert's law (also known as Bouguer's law) which states that layers of equal thickness of the same substance transmit the same fraction of incident light, at any given wavelength. The second is Beer's Law which states that the absorption of light is proportional to the number of absorbing molecules in its path (i.e. the concentration of the absorbing solution). These laws can be combined to form

the Beer-Lambert law, which can be expressed mathematically thus:

$$I = I_0 10^{-\varepsilon c l}$$

where I is the intensity of the transmitted radiation, I_0 is the intensity of the incident radiation, ε is the molar extinction coefficient (l mol^{-1} cm^{-1}), c is the concentration of the absorbing substance (mol l^{-1}) and l is the path length through which the radiation passes (cm). In Figure 2.4, I_0 is the intensity of the radiation entering the fibre and I is the intensity at the point where the ray is about to emerge from the fibre.

When the percentage of incident light transmitted (T) is measured, the above expression can be written:

$$A = \log (100/T) = \varepsilon c l$$

where A is the absorbance.

Deviations from the Beer-Lambert law can occur if the dye is aggregated, rather than dissolved as monomolecular species within a fibre.

Reflection from multiple fibres

With most textiles, a substantial proportion of the total incident light actually penetrates the surface and undergoes multiple absorption and scattering processes within the textile material. Most of the diffusely scattered component of the light which emerges from the surface has undergone multiple absorption and scattering processes as the light passes through the fibres from which the textile is composed. This is illustrated in Figure 2.5 which shows how a ray of light can be reflected from fibre surfaces, and undergo absorption within fibres, as it is scattered within an array of fibres.

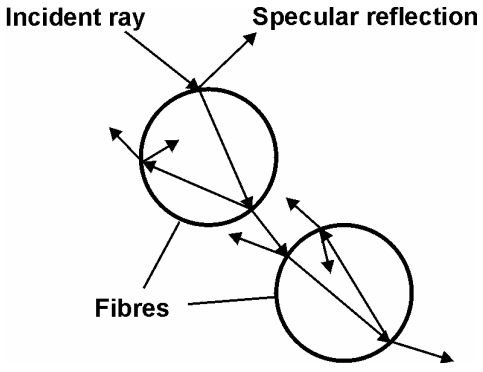

Figure 2.5 Possible reflection, scattering and absorption processes within fibres

Generally, when the reflectance spectra of textiles are measured the samples are made sufficiently thick so that no light penetrates the full thickness of the sample. This eliminates any extraneous contribution from the sample backing.

The Kubelka-Munk function

The Kubelka Munk equation gives the relationship between absorption, scattering and reflectance of a sample at a particular wavelength as follows:

$$K/S = \frac{(1 - R_\infty)^2}{2R_\infty}$$

and

$$R_\infty = (K/S + 1) - \sqrt{[(K/S + 1)^2 - 1]}$$

where K is the absorption coefficient, S is the scattering coefficient, R_∞ is the reflectance of the surface having such a thickness that there is no further change in the reflectance by increasing the thickness. R_∞ is often given simply as R and the ratio K/S as θ because the individual values of K and S are never actually determined in ordinary colour measurements. To ensure that reflectance values are equal to R_∞, samples should be checked to ensure that they fulfil this condition, particularly if the measurement is to be used for quantitative purposes. It is usual to fold fabric samples into a number of layers, until constant readings are obtained. At least four thicknesses are commonly required. The reflectance value R is expressed as a decimal fraction.

For dark shades when samples with very low reflectance at particular wavelengths, the equation can be modified and R_∞ replaced by a corrected value: $R_\infty = R - R_0$

$$K/S = \frac{[1 - (R - R_0)]^2}{2(R - R_0)}$$

where R is the measured value of reflectance at a particular wavelength and R_0 is the minimum value of reflectance obtained with the deepest possible dyeing at that wavelength of maximum absorption with the dye or dyes under examination.

As shall be demonstrated later, the K/S values are additive functions which can be related to dyestuff concentrations. Thus the Kubelka-Munk theory is to fabric what the Beers-Lambert law is to solutions.

Standard conditions for illumination, viewing and measurement

The specular component is not wavelength dependent, but the diffuse component is and, as has already been discussed, will depend on the absorption and scattering characteristics of the sample and of the distribution and type of

any colorants contained in the substrate. Generally both the specular and diffuse components will vary with the direction of illumination and viewing. Samples such as paint films, films of printing inks and the surfaces of plastics articles can range from smooth and glossy to semi-matt and matt. Textile samples show a much greater range depending on the nature of the fibre, natural or man-made, the contour of the fibre surface, whether or not the fabric is de-lustered, the twist of the yarn and the construction of the fabric. At one end of the range lie such fabrics as continuous filament nylon in a sateen weave, and at the other hand-knitted wool garments. Some different surface scattering properties are illustrated in Figure 2.6.

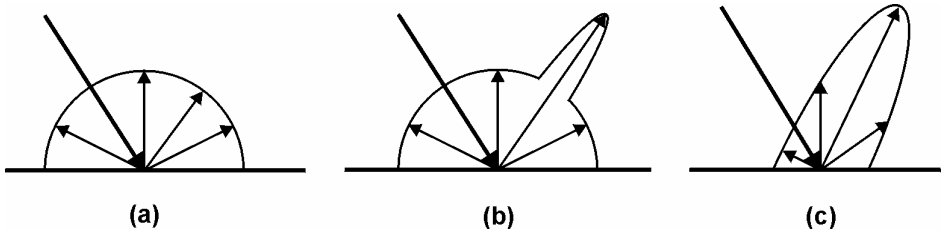

Figure 2.6 Different surface scattering characteristics;
(a) matte surface - most light is diffusely reflected,
(b) eggshell finish - some light is specularly reflected,
(c) glossy finish - most light is specularly reflected

These problems were not well recognised in the 1931 CIE system, where it was merely specified that for reflectance measurements the sample should be illuminated at 45^o to the normal and viewed normally, i.e. at 90^o to the surface.

It was soon recognised that reflectance from semi-glossy surfaces was most simply measured by collecting all the light reflected from a sample using an integrating sphere or by illuminating the samples diffusely and observing the sample approximately in the normal direction. An integrating sphere, has its inner surface painted a matte white usually using a barium sulphate based paint. Radiation is diffused from the inner surface of the sphere by multiple paths, as illustrated in Figure 17. It has also been stipulated that in any beam the angle between the axis and any constituent ray should not exceed 5^o.

Four sets of conditions are now recommended. These are 45/0, 0/45, d/0 and 0/d. The various modes are illustrated in Figure 2.7.

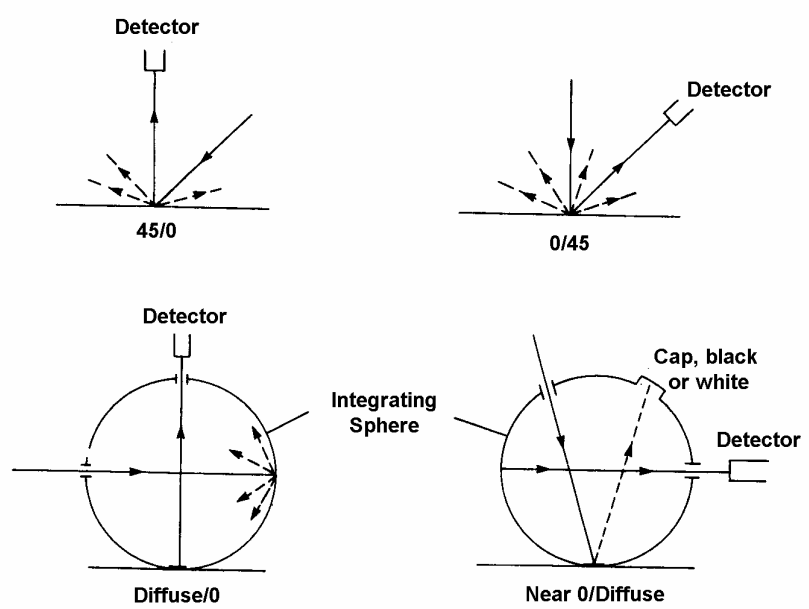

Figure 2.7 Schematic diagrams of common illuminating and viewing conditions in spectrophotometry

Using near 0/d or d/near 0 geometry it is possible to exclude the specular component, if that is required. Usually the beam from the source or the detector is at a small angle to the normal (typically 8^{o}) and this makes it possible to insert a black cap in the side of the integrating sphere at a position to block the specular component from the sample. To include the specular component the cap is replaced by a white reflector which matches the inside of the sphere.

It is assumed that the results from the two sets of conditions (1) 0/45 and 45/0 and (2) d/0 and 0/d, should be equivalent and this is generally true because polarised light is not commonly encountered in colour matching situations.

Measurement of textile samples is usually carried out with integrating spheres of around 100 mm diameter, to ensure adequate averaging over surfaces which can be somewhat uneven. Paint and paper samples can be measured accurately using smaller spheres because of the more even surfaces usually encountered.

Measurement of the reflectance of fluorescent materials

A fluorescent sample absorbs radiation in the ultraviolet wavelength region of the spectrum and re-emits some of the absorbed energy at a longer wavelength in the blue region. When a sample is illuminated with a source which emulates illuminant D_{65} it will fluoresce because of the ultraviolet component in the illuminating radiation (see Figure 5). On the other hand, if a source which emulates illuminant A is used, the sample will not fluoresce because of the absence of ultraviolet radiation (see Figure 5). When spectra of a single sample illuminated by the two different sources are compared, any fluorescent component will become apparent. This can be the basis of the measurement of

fluorescent materials. Of course the scientifically precise measurement of fluorescence is not possible with the normal type of reflectance spectrophotometer - a special double monochromator instrument is required. (Samples are illuminated with monochromatic radiation and the spectrum of the scattered radiation is obtained then using stepwise changes in the wavelength of the incident radiation, the full relationship between the exciting radiation and the resulting fluorescence is built up.)

Trichromatic colorimeters

While reflectance spectrophotometers are essential for recipe prediction and colour correction work trichromatic colorimeters can be used to obtain tristimulus values and are useful for simple quality control and colour difference measurements.

Before the advent of microprocessor technology, trichromatic colorimeters were widely used to carry out the integration needed to convert reflectance into tristimulus values by optical methods. They comprise a light source, a series of wide-band filters (generally three or four) and a detector with an amplifier coupled to an output device. Figure 2.8 shows a basic instrument of this type.

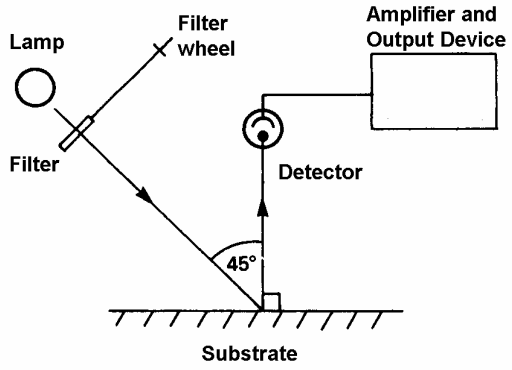

Figure 2.8 A typical tristimulus colorimeter

The filters are constructed so that their transmission characteristics match the eye sensitivity functions for the 2^o or 10^o CIE standard observers. The filters in the light path can be changed in succession and data processed by simple electronic circuitry. In combination with a calibrated source of illumination, tristimulus values can be obtained after calibration of the instrument with an appropriate white standard. By including simple calculation software, CIELAB data can then be output and colour differences can be calculated by measuring successive samples.

Colourimeters providing optical integration within the instruments once had advantages over spectrophotometers in terms of cost, ruggedness and simplicity of operation. This type of colour measuring instrument found wide use in industrial control applications. However, tristimulus colourimeters have become superceded by recent developments in spectrophotometer technology

linked with the use of microprocessors.

Reflectance spectrophotometers

Many of the spectrophotometers used for reflectance measurements even up to the 1960s were not very satisfactory because they were originally designed as spectrophotometers for transmission measurements in the ultraviolet and visible regions, and reflectance attachments were added as an afterthought and as 'optional accessories'. The photometric accuracy of these instruments was not high and they were not satisfactory for colour measurements. The beam intensities were not high enough for rapid measurements and the measurement geometry did not permit efficient diffuse illumination or diffuse measurement conditions or efficient removal of the specular component of the sample reflectance. The widespread use of colour measurement and recipe prediction methods by industry had to await the development of suitable purpose-built colour measuring instruments.

Many types of reflectance spectrophotometers have been developed in the last 30 years. The most important changes in the design reflectance spectrophotometers have been:

- Very substantial improvements in electronic stability of detectors, electronic miniaturization and the use of digital signal processing of have made it possible to produce simple and robust instruments with single or dual optical paths.
- Use of approximate d/0 geometry with CIE-specified sources has made it possible to measure fluorescent samples accurately.
- Replacement of prism and grating monochromators, and narrow-band interference filter wheels, with gratings combined with solid state detector arrays, combined with illumination of samples with high intensity discharge lamps make it possible to obtain measurements in no more than a few seconds.

An example of a modern-type reflectance spectrophotometer is shown in Figure 2.9. This is the Macbeth MS2020 spectrophotometer. The sample to be measured is diffusely illuminated with heterochromatic flash of radiation from a high-pressure xenon arc flash tube mounted on a port on the side of the integrating sphere. The radiation is filtered to approximately emulate illuminant D_{65}. Radiation reflected from the sample at 8^o to the normal is collected and dispersed by means of a diffraction grating and the spectrum is passed to an array of 18 solid state detectors covering the range 380-700 nm. A reference signal is obtained from a detector that samples the diffuse illuminating radiation by viewing the inside wall of the integrating sphere. The resulting reflectance data pass to a microprocessor which produces an output of data in any required form within a few seconds. The data may be fed directly to a computer for further processing before being displayed and stored. The instrument is calibrated from time to time by measuring a reflectance standard. The specular component of reflectance can be excluded by replacing the ‘specular port’ on the integrating sphere, at 8^o to the normal and at a

complementary angle to the measurement port, with a black trap.

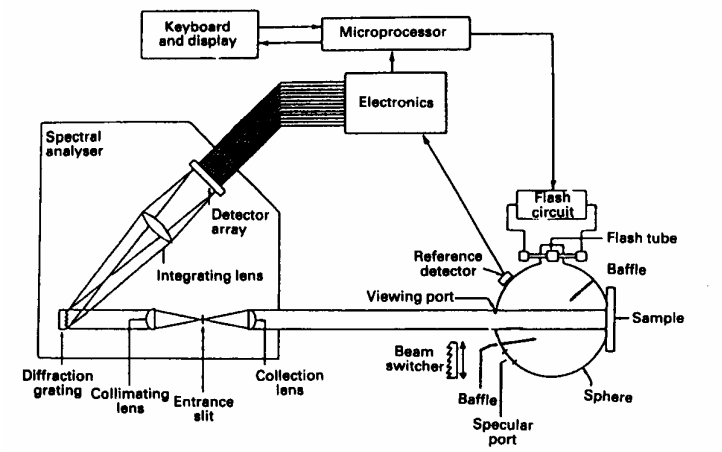

Figure 2.9 A schematic diagram of the Macbeth MS2020 spectrophotometer

Sample presentation

Samples must satisfy the thickness criterion for K/S measurement. Fabric is normally folded at least twice. Yarn is usually wound on a card to form a thick, even, wad. Loose fibre can be felted into a pad or placed in a cell with a transparent window, as illustrated in Figure 2.10.

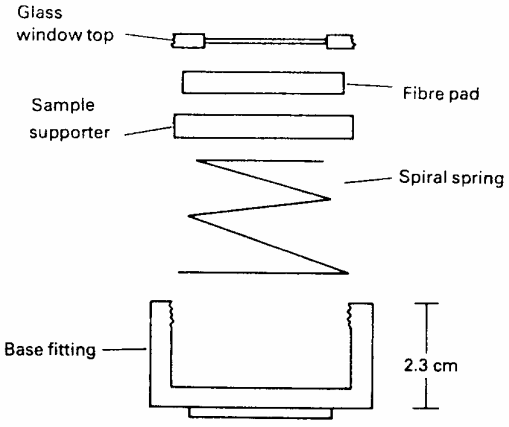

Figure 2.10 A cell for measurement of the colour of loose fibres

Yarn and loose fibre may be measured with the fibres end-on by drawing the fibre or yarn into a tube of suitable diameter to form a dense plug and the end of the plug is then trimmed flat using a very sharp blade.

Reflectance standards

The CIE recommends that reflectance measurements should be made relative to a perfect diffuser, i.e. a sample that diffusely reflects all the light incident upon it. No such surface exists, but working standards of known spectral

reflectance factors are normally used. (For example, if the working standard reflects 98% of the light of a particular wavelength all values measured relative to the working standard need to be multiplied by I00/98.) Formerly magnesium oxide and barium sulphate were used as reference standards but they were often fragile and prone to yellowing. Recently, standards made from opaline glass have become available. They are very white, stable and relatively robust and are the standards of choice.

The tristimulus values of a perfect reflecting white diffuser as determined for the CIE 10^o observer are given in Table 3.

Table 2.2 Tristimulus values of a perfect reflecting diffuser for the 10^o observer

Illuminant	X_n	Y_n	Z_n
A	111.1	100.0	35.2
C	97.3	100.0	116.1
D_{65}	94.8	100.0	107.3

A further check on accuracy and reproducibility of a reflectance spectrometer can be carried with permanent standards. Suitable ceramic or enameled tiles are produced by standards organisations for this purpose. For example, sets of coloured ceramic tiles in various colours, including grey, are produced by the British Ceramic Research Association. If required, they can be individually calibrated by the British National Physical Laboratory.

Review questions

1. *Explain the difference between a colourimeter and a spectrophotometer.*
2. *What are the factors to be considered in choosing the measurement geometry of a spectrophometer for textiles?*
3. *What are the laws which determine the amount of light reflected from the surface of a textile?*
4. *How can the thickness of a sample affect the measured reflectance? How can an appropriate thickness for reliable measurements be determined?*
5. *What is the difference between specular and diffuse reflection?*
6. *What are the features of a modern spectrophotometer which allow measurements to be made very quickly?*

Topic 3.

Specification of colour

Introduction

The use of colour measurements and the evaluation of colour differences are crucial to effective quality control in the colouration industry. The need to communicate by colour and to agree on colour tolerances in production is becoming increasingly crucial to commercial profitability.

Objectives

At the end of this topic you should be able to:

- *appreciate the use of colour atlases to specify colours,*
- *understand how chromaticity coordinates have been transformed in various ways to create uniform colour spaces,*
- *know how CIELAB colour space is defined and how it is used to specify colours and colour differences,*
- *understand how whiteness of textiles is specified.*

Colour Atlases

Before the advent of instrumental colour measurement, it was usual for a supplier and customer to rely on agreed physical standards which were assessed visually. In textiles this was usually an actual sample of a colored fabric (or yarn). Most manufacturers built up a large library of coloured samples. However, most textile collections of swatches fell well short of all possible textile color gamuts. Problems with fading and soiling developed a tendency to rely on non-textile standards of a more permanent nature.

The role of the colour atlas is to create a representation and notation of colours which can be used to conduct a less subjective dialogue than is possible with words alone. In addition they seek to provide a rational method of systematically arranging equally-spaced samples of all possible colours. These atlases have been used for colour specifications when suitable samples on the substrate to be matched are not available. It is accepted practice to compare, textiles, paints, printing inks, ceramics and even bird feathers to the coloured chips in a colour atlas. Colour atlases are sometimes still encountered and will be briefly described for the insights which they provide into the problems of colour specification.

There are many ways in which colours can be described but there are three common features which are described to classify colours in three-dimensional colour space. These are:

- hue,

- purity or saturation,
- lightness or darkness.

Hue is the attribute of colour sensation which gives rise to colour names, such as red, yellow, orange, green, blue, purple and so on. Most of these colours can be represented by a single wavelength of visible light.

Purity or saturation describes the visual sensation related to the strength of the colour. It is independent of hue and can be represented on a scale varying from white to pure colour.

Lightness or darkness is the visual sensation related to the brightness of a colour. It can be rated on a scale varying from white to black. It is independent of hue and saturation.

Of course, color atlases can be allied with instrumental methods of matching colors. ICI was the first to experiment with this approach. Currently, colour atlases are being superceded by the use of calibrated colour computer monitors to display colour samples. This VDU method can be easily linked to instrumentally measured colour parameters and used for many purposes such as colour matching and shade specification. “Virtual” colours can be easily created by computer software without the need for a coloured sample. As yet there is no standard method for viewing and comparing real samples with colours displayed on a VDU screen. Standard illumination conditions should be used for visual comparisons between chips in a colour atlas and textile samples.

A frequent problem with shades in a colour atlas, or colours viewed on a computer screen, is that it is seldom possible to achieve an exact match on a real textile substrate. This is because it is not possible to use the same colourants to create the colours on the textile as are used in a colour atlas or on a computer screen. Indeed, colours on a VDU are created by an additive process involving light emitting phosphors and pigments are used to colour the chips of colour atlases, whereas dyes or pigments are used on textiles. Under these circumstances metamerism is always likely to occur. Matching between polyglot samples or media is also complicated by the fact that the surface reflectance characteristics are usually different.

The most well-known collections of coloured samples include the following:

- The Dictionary of Colour (A. Maerz and M. R Paul, McGraw Hill, New York, 1930)
- The Colour Harmony Manual (Oswald)
- The ICI Colour Atlas (ICI)
- Pantone Colour System (Colour marketing Group, USA)
- DIN Colour Chart (M Richter, Farbe **1** (1953a) 85)
- Munsell System (Munsell Colour Co.)
- Normacolour Spatial System (M—canorma).

The Munsell Colour system has been very popular, particularly in the USA. This book consists of colour samples (or chips) spaced on the order of 20 just-perceptible differences apart. Colors not illustrated in the books can be specified by extrapolation and by interpolation. Read Rivlin (1992) Section 4.3 for an introduction to the Munsell System.

Make sure you understand the terms Munsell value, chroma and hue and how these are used to arrange the color samples in the Munsell System in a systematic manner.

How chromaticity colour coordinates are used in practice

While the tristimulus values X, Y and Z completely specify the physical colour of any substrate, when the values of a large number of colours are plotted in three-dimensional space, a very confusing picture emerges. The arrangement of colours is not orderly as in the Munsell System and differences in colour are not evenly spaced. In 1931, in an attempt to produce a more orderly system, the CIE also introduced the concept of chromaticity coordinates x, y and z. These are defined as follows:

$$x = \frac{X}{X+Y+Z} \quad , \quad y = \frac{Y}{X+Y+Z} \quad , \quad z = \frac{Z}{X+Y+Z}$$

where $x + y + z = 1$. It therefore follows that if x and y are known, then z can be calculated. The two-dimensional plot of x versus y is called the chromaticity diagram as shown in Figure 3.1.

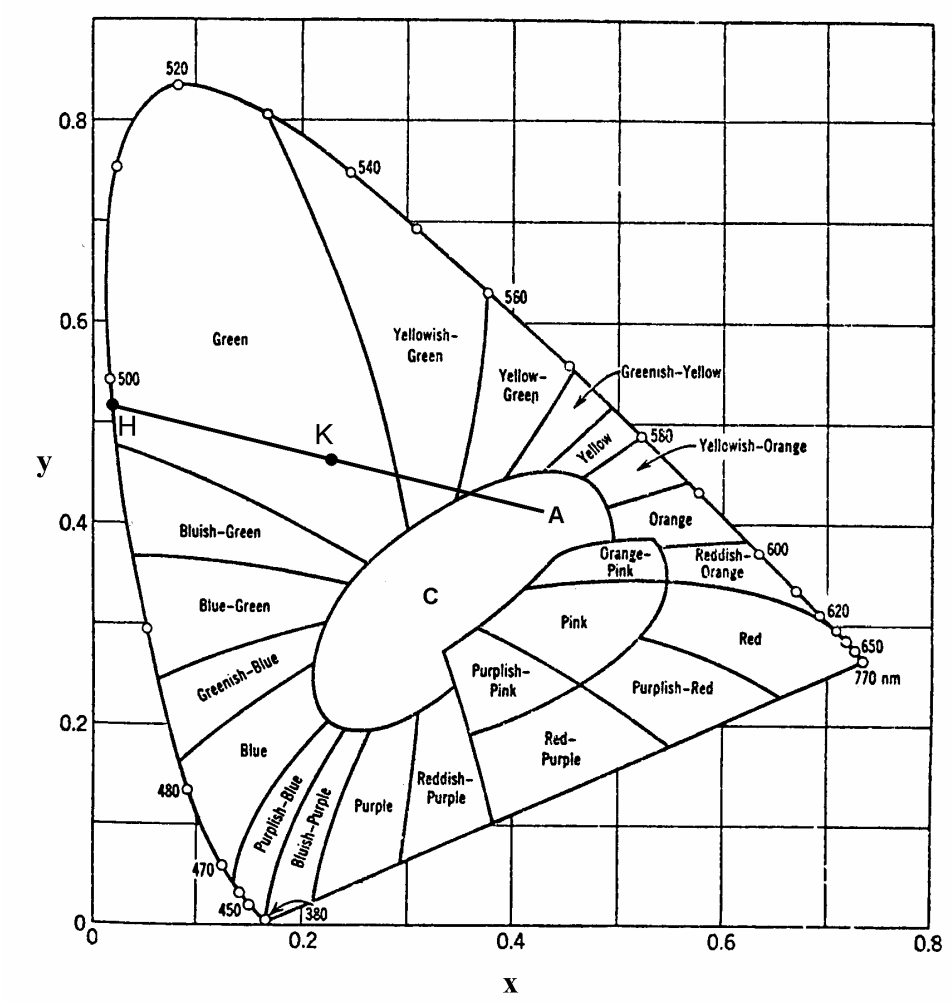

Figure 3.1 The CIE chromaticity diagram

In this diagram, colours are found to be arranged in a logical order. Similar colours are grouped together. Near the centre is white, as defined by the illuminant used for the determination of the tristimulus values. The effect of changing the illuminant is to move the position of the "white point" on the diagram. The positions of illuminants A and C are shown on the diagram. Moving away from the centre of the diagram, the colours become purer and stronger. Lines of constant hue are not always straight The outer boundary of visible colours forms an envelope called the spectrum locus. The wavelength equivalent to each colour is shown on the outside of the envelope. This is called the dominant wavelength. Note that some colours do not have equivalent dominant wavelengths. All known colours can be depicted on the diagram and defined by x, y and z values. Using the diagram it is possible to determine the dominant wavelength and colourimetric purity of any colour, given the chromaticity coordinates of the colour determined under a particular illuminant. The dominant wavelength is found by drawing a line from the point representing the chromaticity coordinates of the source under which the tristimulus values were measured, through the point representing the

chromaticity coordinates of the sample colour and producing it to the spectrum locus. The colourimetric purity is the percentage distance of the point representing the chromaticity coordinates of the sample colour from the point representing the chromaticity coordinates of the source, relative to the distance of the point on the spectrum locus representing the dominant wavelength of the colour from the point representing the chromaticity coordinates of the source. In Figure 21, a green colour represented at K for which x = 0.230 and y = 0.465 measured under illuminant A has a dominant wavelength at H of 499 nm and a colourimetric purity of 50% given by 100(AK)/(HA).

It is obvious that colours are not evenly arranged in the chromaticity diagram. In other words, linear distances between points on the diagram do not correspond with the magnitude of perceived colour differences. Hence, while chromaticity diagrams are useful for specifying colour they are not particularly suitable for describing the perceived differences between colours. In order to do this, further transformations of tristimulus values are required to obtain some sort of uniform colour space.

MacAdam ellipses and their applications

In 1942 MacAdam published a study in which he sought to plot areas of equal colour perception on the chromaticity diagram (D L MacAdam, J. Opt Soc. Amer., **32** (1942) 247). He designed a split-field visual colorimeter so that an observer could vary the colour of one half of a 2^o field along a straight line in the xy diagram and find the limits to which the xy values could be changed before the colour changed perceptibly relatively to the colour in the other half of the field, while the luminance was kept constant. The orientation of the straight line could be varied and the observer made repeated matches against 25 points throughout the *xy* diagram. MacAdam plotted the standard deviation of matches along each line and found that the points lay on ellipses. The resultant diagram is shown in Figure 3.2.

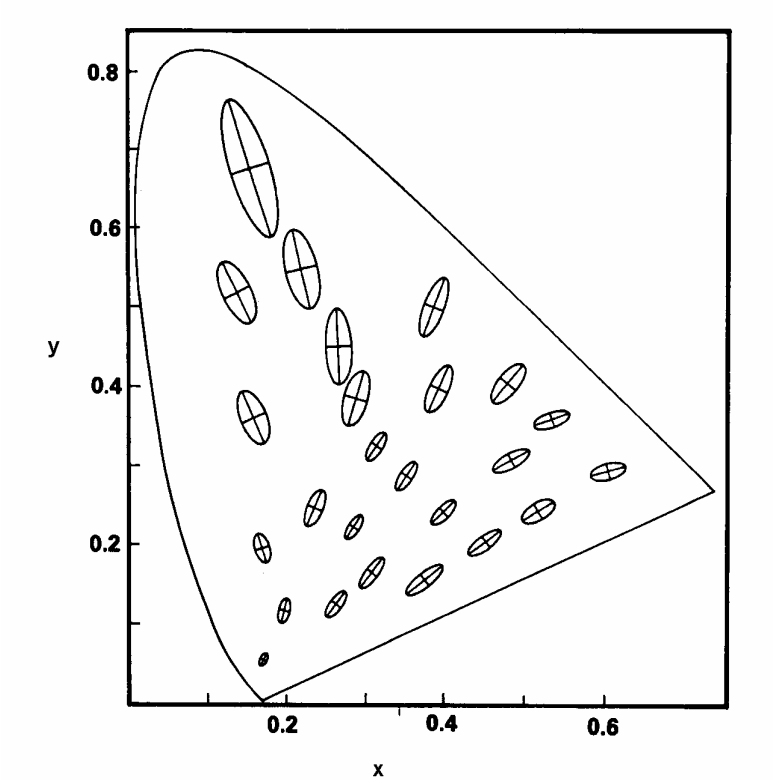

Figure 3.2 MacAdam ellipses plotted ten times their actual size on a CIE 1931 chromaticity diagram

Further experiments indicated that a just perceptible colour difference was about three times larger than the standard deviation of colour matching. It can be seen that the spacing of colour differences in the chromaticity diagram varies considerably but in a consistent manner. The data obtained by MacAdam could be used for calculating quantitative colour differences, provided they were not too great. A useful method was devised by Simon and Goodwin who drew up charts for different regions of the *xy* diagram in which the x any y axes were plotted at angles so that the ellipses were transformed into circles and the axes were scaled so that linear distances represented chromaticity differences in MacAdam units (F T Simon and W J Goodwin, Amer. Dyestuff Rep., **47** (1958) 105). A typical chart is shown in Figure 3.3.

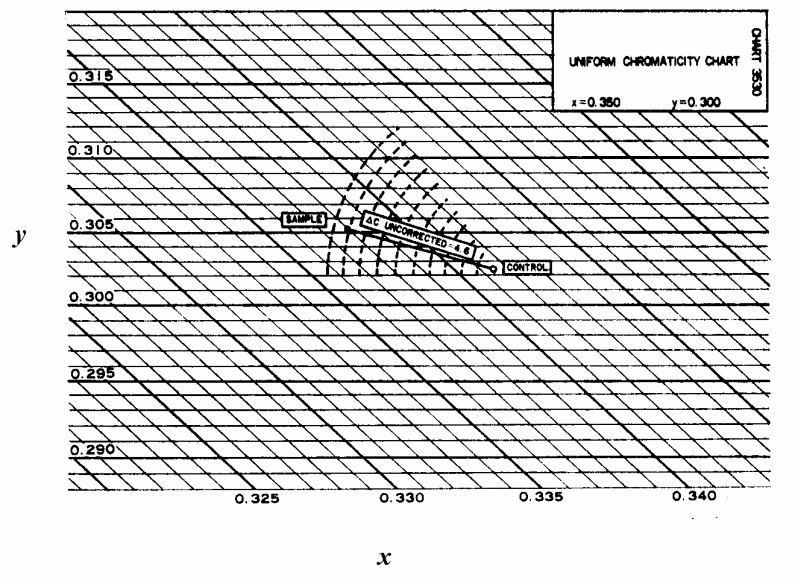

Figure 3.3. A Simon-Goodwin chart for obtaining colour differences from measurements of chromaticity coordinates

Friele, MacAdam and Chickering developed colour-difference equations based on MacAdam's data which were known as FMC-1 and FMC-2 (K Chickering, J. Opt. Soc. Amer., 58 (1967) 537). The latter contains a function to take the Y value into account. For a time this was the most popular equation in the USA. Equations based on MacAdam ellipses have been superceded by subsequent developments adopted by the CIE.

CIELAB colour space

In 1976 the CIE introduced the L*, a* and b* chromaticity coordinates and these are now widely used.

$$L^* = 116\,(Y/Y_n)^{1/3} - 16$$

$$a^* = 500\,[(X/X_n)^{1/3} - (Y/Y_n)^{1/3}]$$

$$b^* = 200\,[(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}]$$

where Xn, Yn, and Zn are the tristimulus values for the relevant standard illuminant and observer. These equations only apply provided X/X_n, Y/Y_n and $Z/Z_n > 0.008856$.

When X/X_n, Y/Y_n and Z/Z_n Ω 0.008856, that is for very dark colours:

$$L^* = 903.3\,(Y/Y_n)$$

$$a^* = 3893.5\,[(X/X_n) - (Y/Y_n)]$$

$$b^* = 1557.4\,[(Y/Y_n) - (Z/Z_n)]$$

When the L*, a* and b* values are plotted in three dimensions the colour space obtained is visually more uniform than in the chromaticity diagram. A representation of CIELAB colour space is shown in Figure 3.4.

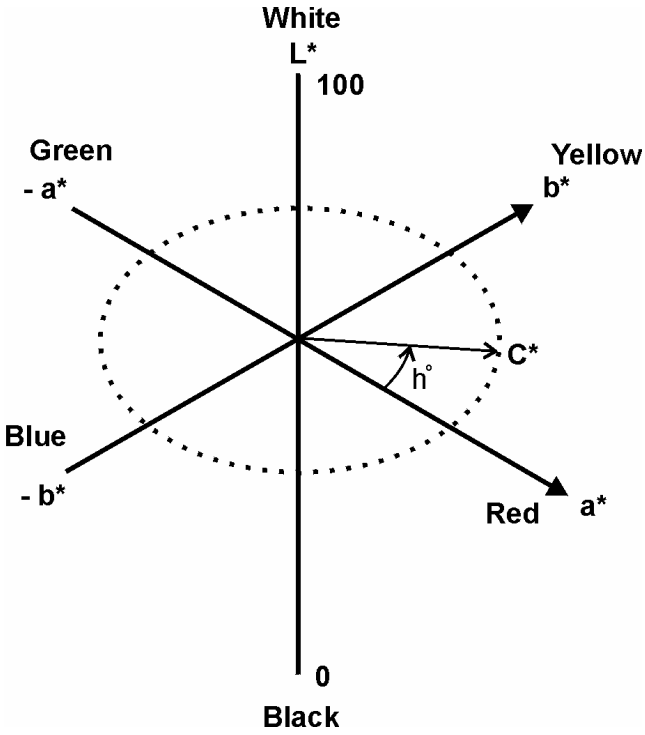

Figure 3.4 CIELAB colour space

L* values are a measure of lightness and vary from zero for black and 100 for white. Positive values of a* give a measure of redness while negative values correlate with the green sensation. Positive b* values indicate the strength of the yellow component and negative values the strength of the blue. The distance of the colour coordinates from the L* axis is a measure of the colour strength, saturation or chroma which is given the symbol C*, and the angle h in the a*b* plane is a measure of the hue. Note that there are no such colours as yellow-blue or red-green.

Thus the CIELAB values expressed in cylindrical coordinates are as follows:

$$C^* = [(a^*)^2 + (b^*)^2]^{1/2}$$

$$h = \arctan (b^*/a^*)$$

The CIELAB colour difference (ΔE^*) between two samples (1 and 2), with coordinates L^*_1, a^*_1, b^*_1 and L^*_2, a^*_2, b^*_2, is the linear distance between the coordinates and is given by:

$$\Delta E^* = [(L^*_1 - L^*_2)^2 + (a^*_1 - a^*_2)^2 + (b^*_1 - b^*_2)2]^{1/2}$$

$$= [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

A CIELAB ΔE^* value of one unit was originally supposed to represent the smallest colour difference which could be visually detected. However, subsequent experience has shown that the visual detection limit is more like 0.8 of a CIE unit.

Where Δa^* is the red-green colour difference and Δb^* is the yellow-blue colour difference. When Δa^* is positive, sample 1 is more red; when Δa^* is negative, sample 1 is more green; when Δb^* is positive, sample 1 is more yellow; when Δb^* is negative, sample 1 is more blue; when ΔL^* is positive, sample 1 is lighter; when ΔL^* is negative, sample 1 is darker.

The chromaticity difference Δc is also sometimes used as a measure of the variation not due to changes in lightness.

$$\Delta c = [(\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

CIELAB colour space is still not quite visually uniform and other transformations of tristimulus data have been used to produce more uniform results. One that has received some attention is CIELUV colour space but it has not proved as popular as the simpler CIELAB formulae. The CIELUV parameters are defined as follows:

$$L^* = 116\left(Y/Y_n\right)^{1/3} - 16$$
$$u^* = 13L^*\left(u' - u'_n\right)$$
$$v^* = 13L^*\left(v' - v'_n\right)$$

where $u' = 4X/(X+15Y+3Z)$ and $v' = 9Y/(X+15Y+3Z)$ and u'_n and v'_n are the u' and v' values calculated using X_n, Y_n and Z_n respectively.

Colour differences in CIELUV colour space are given by:

$$\Delta E = \left[(\Delta L^*)^2 + (\Delta u^*)^2 + (\Delta v^*)^2\right]^{1/2}$$

Grey scales

Colour changes in fastness and staining tests are usually rated visually against gray scales. Two scales are commonly used: one for assessing changes in shade and one for assessing staining. These scales are available from organisations such as the Society of Dyers and Colourists (SDC) and the American Association of Textile Chemists and Colourists (AATCC).

The colour difference scale consists of pairs of gray specimens. The scale is used by matching a change in lightness of a sample relative to a reference (such as comparing a washed with an unwashed fabric sample). If a change in hue is noticed (yellower, redder, etc.) this is normally also noted when the results are given.

The staining scale is a series of grey plaques used to assess the lightness of a staining sample relative to an unstained reference. Sometimes it is difficult to assess the staining of coloured samples (for example in a rubbing fastness test) so the AATCC has released a series of coloured plaques to assist with this assessment.

The colour differences between the various gray plaques are given in Table 3.1.

Table 3.1 CIELAB colour differences corresponding to colour changes on the standard gray scales, according to ISO recommendations

Grade	Effect scale ISO 105-A02	Staining scale ISO 105-A03
5	0	0
4-5	0.8	2.2
4	1.7	4.3
3-4	2.5	6.0
3	3.4	8.5
2-3	4.8	12.0
2	6.8	16.9
1-2	9.6	24.0
1	13.6	34.1

Measurement of whiteness

Many whiteness formulae have been published. The need for whiteness assessment arises because tristimulus measurements alone do not give a good indication of whiteness, particularly for very white, highly reflective, materials.

In 1982 the CIE published a whiteness index, W, which is now a benchmark for other estimates.

$$W = Y + 800(x_n - x) + 1700(y_n - y)$$

where x, y and Y are the appropriate chromaticity and tristimulus values under illuminant D_{65} and x_n and y_n are the chromaticity coordinates of the light source under which the sample is viewed.

A perfectly white material will have a W value of 100. However, samples treated with fluorescent whitening agents can give values as high as 150. Fluorescent whitening agents do not increase the reflectivity (Y value) of a

sample but increase the amount of scattered blue light, when they are viewed in daylight or under a source with a suitable ultraviolet component. This has the effect of making the sample appear very white. Fluorescent whitening agents absorb light in the ultraviolet region and re-emit it in the blue region of the spectrum.

Yellowness Index

The degree of yellowness of raw (un-scoured) wool has been specified in many different ways. Sometimes the Y value or Y-Z is quoted. The yellowness index (YI) also has been widely used. It is sometimes defined as:

$$YI = 100(X-Y)/Y$$

The most suitable formula has been defined by the American Society for Testing Materials (ASTM) in their Test Method D1925 as:

$$YI = \frac{128X - 106Z}{Y}$$

The whiter the substrate, the lower the yellowness index.

Review questions

1. *When would a colour atlas be used in preference to any other method of specifying colour?*
2. *What is the dominant wavelength of a colour, and how is it determined from tristimulus values?*
3. *What is the relationship between MacAdam ellipses and Simon-Goodwin charts?*
4. *What is the advantage of the CIELAB system over the chromaticity diagram for determining colour differences?*
5. *Why is whiteness assessed by special formulae?*

Topic 4.

The use of colour measurement in practice

Introduction

The use of colour instrumental measurement methods in industry involves a considerable investment in equipment, training of operators and in time taken to collect data. This can be repaid many times over in terms of improved economy and greater efficiency in processing and in increased customer satisfaction.

Objectives

At the end of this topic you should be able to:

- *explain how colour differences are assessed and used in practice,*
- *define the terms metamerism and colour constancy,*
- *recount the requirements for viewing coloured samples in the laboratory,*
- *understand how K/S values are related to dye concentration,*
- *appreciate how instrumental match prediction and colour correction are carried out.*

What is a match?

The reliability of over 100 professional shade passers in the UK and USA has been assessed and it was found that 17% of the single colour matching decisions were rated as wrong by a majority of the people who assessed the samples. The mistakes were equally split between passing a dyeing which should have been shaded and shading a dyeing which was already within commercial tolerances. This level of inconsistency obviously increases costs of dyeing, because of unnecessary re-dyes, and also may incur penalties from customers because of off-shade batches. The only long-term solution is to replace subjective assessment with instrumental shade passing. However, when single-value CIELAB colour differences were applied to a large amount of visual data, it resulted in more wrong decisions than the average professional shade passer. Colour-difference measurements showed that under industrial conditions there is a greater tolerance towards depth and/or brightness variations than towards variations in hue. At present, it seems that colour difference based shade passing can only be achieved by mapping the departures from uniformity and devising methods of allowing them to be incorporated into colour-difference calculations. Two such systems are currently in use.

The CMC conformity system

A number of complex algorithms have been developed by companies such as J&P Coates and Marks and Spencer for in-house use, but the best known is the so-called CMC (l:c) equation:

$$\Delta E = \left[\left(\frac{\Delta L^*}{l S_L} \right)^2 + \left(\frac{\Delta C^*}{c S_C} \right)^2 + \left(\frac{\Delta H^*}{S_H} \right)^2 \right]^{1/2}$$

where $\Delta H^* = [(\Delta E)^2 - (\Delta L^*)^2 - (\Delta C^*)^2]^{1/2}$
$S_L = 0.040975 L_1^*/(1+0.01765 L_1^*)$ unless $L_1^* < 16$ then $S_L = 0.511$
$S_C = 0.0638 C_1^*/(1+0.0131 C_1^*) + 0.638$
$S_H = S_C(Tf + 1 + f)$
$f = \{(C_1^*)^4/[(C_1^*)^4 + 1900]\}^{1/2}$
$T = 0.36 + |0.4 \cos(h_1 + 35)|$
unless $164^o < h_1 < 345^o$ then $T = 0.56 + |0.2 \cos(h_1 + 168)|$
and L_1^*, C_1^* and h_1 refer to the standard.

The various constants are chosen so that l and c are set equal to unity and in this case the equation is referred to as the CMC (1:1) formula. This formula is the most reliable yet developed for relating perceived colour differences to instrumental measurements for colour differences up to 10 CIELAB units. It has been developed as a result of data collected from thousands of visual assessments. This formula is under consideration for adoption by the CIE to supercede the simpler CIELAB and CIELUV formulae.

The CIE 1994 acceptability formula

In 1994 the CIE recommended a modified colour difference formula for the evaluation of industrial colour differences. This contains correction factors to the terms for lightness differences, saturation differences and hue differences in the colour difference formula and is known as the “CIE 94 formula”. The colour difference ΔE^*_{94} is given by:

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

where $S_L = 1$, $S_C = 1 + 0.45\ C^*$ and $S_H = 1 + 0.0015\ C^*$ are weighting factors and k_L, k_C and k_H are correction factors. In the textile industry, $k_L = 2$ and $k_C = k_H = 1$. This formula should be referenced as ΔE^*_{94} or CIE 94 and when correction factors other than $k_L = k_C = k_H = 1$ are used, the factors should be specified. Thus for textiles, the appropriate terminology is ΔE^*_{94} (2:1:1) or CIE 94 (2:1:1).

The practical use of colour difference formulae

When a colour-difference formula is to be used for the first time under industrial conditions, the simplest approach is to determine instrumental tolerances by examining many standard/batch pairs as are available. Visual assessments should be made by a number of shade passers familiar with the closeness of match necessary to avoid customer complaints. These assessments should then be sorted according to visual ratings of pass, fail or borderline. Instrumental measurements of the ΔE values should then be compared with the visual ratings and appropriate pass/fail criteria selected along the following lines:

(a) accept - if $\Delta E <$ pass/fail value,
(b) marginal - if pass/fail value $< \Delta E <$ borderline tolerance value,
(c) reject, if $\Delta E >$ borderline tolerance value.

Batches in the marginal category can be carefully reviewed and a decision made about the commercial acceptability of the match. The use of such a system which is mutually agreed between processor and customer can greatly facilitate trading by increasing customer satisfaction and reducing claims against faulty goods.

Metamerism

Metamerism occurs when two colours match under one set of illumination and viewing conditions, but fail to match under a second set of conditions. Such samples are said to be metameric, or to form a metameric pair. Metamerism is always the result of the fact that the reflectance curves for the two coloured objects are different. Usually the reflectance curves of a metameric pair of samples cross at least three times. The reflectance curves of a pair of samples showing slight metamerism is shown on Figure 4.1.

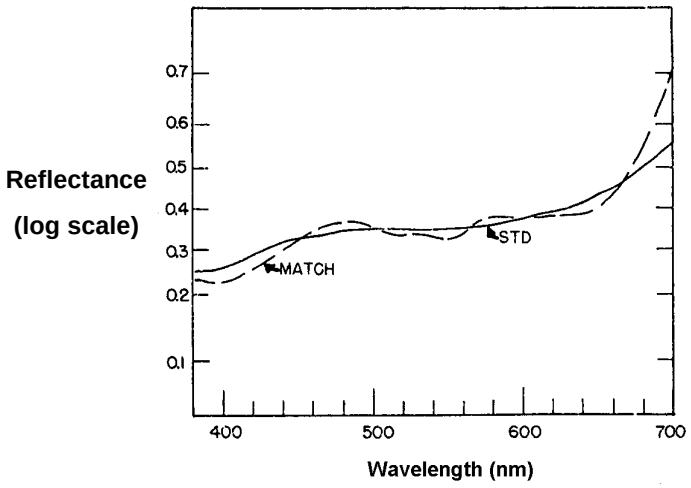

Figure 4.1 The reflectance curves of a metameric pair of samples

In dyeing, it is often possible to match a coloured object (under one specified

set of conditions) using a mixture of three dyes, but the reflectance curve of the dyed sample will not necessarily be the same as that of the object to be matched unless the same dyes as used to produce the original sample can be used. Metamerism can occur to different degrees. A metameric pair may match perfectly under one set of conditions, but be a slight mismatch under other conditions. Such a pair would be said to be slightly metameric. Another pair could match perfectly under one set of conditions, be a slight mismatch under a second set of conditions, but be a very bad mismatch under a third set of conditions. Such a pair would be said to be highly metameric.

Four types of metamerism are recognized:

- illuminant metamerism,
- observer metamerism,
- field size metamerism,
- geometric metamerism.

Illuminant metamerisn is the most common type encountered. In this case, a pair of samples match when viewed under one illuminant (say illuminant D_{65}), but appear different when viewed under another illuminant (say illuminant C). This type of metamerism can be estimated quantitatively using colour difference measurements. The tristimulus values of the two samples under different illuminants can be calculated from the reflectance curves and the CIELAB colour differences between the sample pairs under different illuminants (say A, C, D_{65} and a Philips TL84 lamp) can be used as a measure of illuminant metamerism. A large colour difference under one or two illuminants is a likely indication of severe metamerism. In recipe prediction programs, the likely degree of metamerism of a dye recipe can be predicted before any samples are dyed by calculating the colour differences for the required illuminants.

Observer metamerism is exhibited when a metameric pair matches for one person, but fails to match for a second person. In this case, the wavelength sensitivities of the two people are different and one, or both, may be significantly different to the sensitivity functions of the CIE standard observer. An extreme case of non-standard eye sensitivity is encountered with red-green colourblindness but other types of colourblindness are also possible and as many as 10% of the male population may be affected in some way. Many older people progressively loose sensitivity to the blue end of the spectrum because of changes in the eye. Hence it is possible for the tristimulus values for a metameric pair to be identical when calculated for the standard observer, but the pair may fail to match for a real observer, even when viewed under the correct light source. This can cause problems if the two people are, for example, suppliers and customers. Colour vision tests such as the Munsell 100 Hue Colour Vision test should be used to check the colour vision of all personnel professionally involved in assessing colour.

Field size metamerism occurs when the field viewing angle changes with a single observer, for example from 2^o to 10^o. In this case, a metameric pair may

match when seen at a distance (small field of view) but may no longer match when closer to the eyes (large field of view).

Geometric metamerism occurs when the viewing geometry changes. Metallic paints may match the target colour for one particular angle of illumination and angle of viewing, but no longer match if either angle is changed.

Colour constancy

Colour constancy is a property of a single sample and is the property of objects to appear to be more or less the same colour when viewed under different light sources. Metamerism and colour constancy are closely linked and sometimes confused, but metamerism refers to differences between two samples viewed under different conditions. For example, the visual sensation associated with a white object is similar whether it is viewed in daylight or under incandescent or fluorescent light sources. In fact, the distributions of the wavelengths reflected into the eye are very different in each case. Under incandescent light, the relative amount of light from the red end of the spectrum reaching the eye is much greater than when a white object is viewed in sunlight. The eye and brain compensate for the change of illumination by a process known as chromatic adaptation. One explanation for this process is that we compare the light reflected from an object with that emitted by the light source. If the energy distributions appear to be similar and the reflectance seems high, we judge the object to be white.

We know from experience that while most objects remain more or less colour constant under normal light sources, some objects do change colour appreciably. For example, meat purchased from supermarket cabinets illuminated by fluorescent sources designed to accentuate the redness of meat may appear a much less appealing grey-brown when viewed in natural light coming through the kitchen window.

Despite a considerable amount of work there is still no reliable way of predicting whether an object will be colour constant or how great the apparent change of colour will be under different illuminants. Several different chromatic adaptation formulae using tristimulus values for one illuminant to calculate the corresponding colour for a second illuminant have been proposed but the errors in prediction are too large for the estimates to be useful for practical purposes.

Visual assessment of samples

It is highly desirable that viewing conditions for assessing samples in the colour laboratory be reproducible and as close as possible to standard viewing conditions. In the past, colour matching was carried out in natural diffused light usually coming from a window exposed to the sky in a direction opposite to the sun. This was not very satisfactory because of variations in cloudiness and water vapour content of the atmosphere. Artificial lighting can be used but

the light they may deviate considerably from standard illuminants and make assessment of metamerism difficult. Colour matching cabinets are now commercially available and are a great improvement on natural lighting conditions. The requirements for a good quality colour matching cabinet are as follows:

- working space of at least about 700 cm in width and 40 cm in depth,
- cabinet at a comfortable height so samples can be viewed under approximate d/0 conditions by holding the samples at about 45 degrees at a comfortable reading distance,
- even, diffuse illumination which is no brighter than light entering a south-facing skylight window (southern hemisphere) in summer,
- switch selectable light sources to simulate illuminants A, C or $D_{65,}$ a fluorescent lamp such as TL84 and a UV Blacklight (to reveal the presence of fluorescent dyes and optical brightening agents), as a minimum
- neutral grey walls.

Colour matching cabinets should be situated away from direct light from any other source, preferably with neutral grey surroundings.

The reference viewing conditions for colour matching recommended by the CIE in 1994 are:

- illumination by a source simulating the standard illuminant D_{65},
- lighting of the samples should be at a level of about 1000 lux,
- the environment should be a uniform neutral grey coloured back-ground with lightness $L^* = 50$.

As far as possible, the surfaces to be observed (samples) should satisfy the following conditions:

- the dimensions of the sample and the observation distance should be arranged so that the field of vision is greater than a solid angle of 4 degrees,
- the samples should be placed side by side, so that any lines of separation will be as imperceptible as possible (fabric samples should be oriented with the weave structures in the same direction),
- the structure, texture and color should be as uniform as possible (if pressing is necessary, all the samples should be pressed together and allowed to cool; wool and cotton samples should be conditioned before assessment).

Recipe prediction and colour correction

Computing combined with colour measurement has now brought automated recipe prediction and colour matching within the reach of any medium to large dyehouse. Modern systems can be treated rather as black boxes capable of producing results provided the instructions which came with the equipment are followed carefully. The following discussion is intended to provide an appreciation of the principles behind the processes involved without going too deeply into the sophisticated computational methods which are part of the business of modern colour computing.

The effect of dyestuff concentration on reflectance

The changes in reflectance spectra with the concentration of dyestuff in the substrate are illustrated in Figure 26(a) and Figure 27(d). The relationship is very non-linear and at higher concentrations approaches a constant value. However, when reflectance spectra are converted to K/S spectra, the plots obtained are similar to absorption spectra, as shown in Figure 26(b). Moreover, it is found that the height of the peaks in the K/S spectrum is proportional to the concentration of dye in the substrate at least at lower concentrations, as shown for measurements at 620 nm in Figure 27(e). So, provided the concentration of dye is not too high (say less than about 1-2%) we have the following relationship:

$$K/S = \frac{(1-R)^2}{2R} = kc + a$$

where k is a constant equal to the gradient of the plot of K/S versus concentration, a is a small positive intercept on the K/S axis and c is the concentration of dyestuff. The value of a is actually the K/S value of the substrate which can be written $(K/S)_S$, so:

$$K/S = kc + (K/S)_S$$

When the logarithm of the K/S values is plotted against wavelength, the resulting curves are found to be parallel. This feature is useful in colour calculations and can also be used to check for anomalies in colour data. When K/S versus concentration data are plotted on log/log scales, a strait line is obtained over the usual concentration range for dyes on textiles, as shown Figure 4.3.

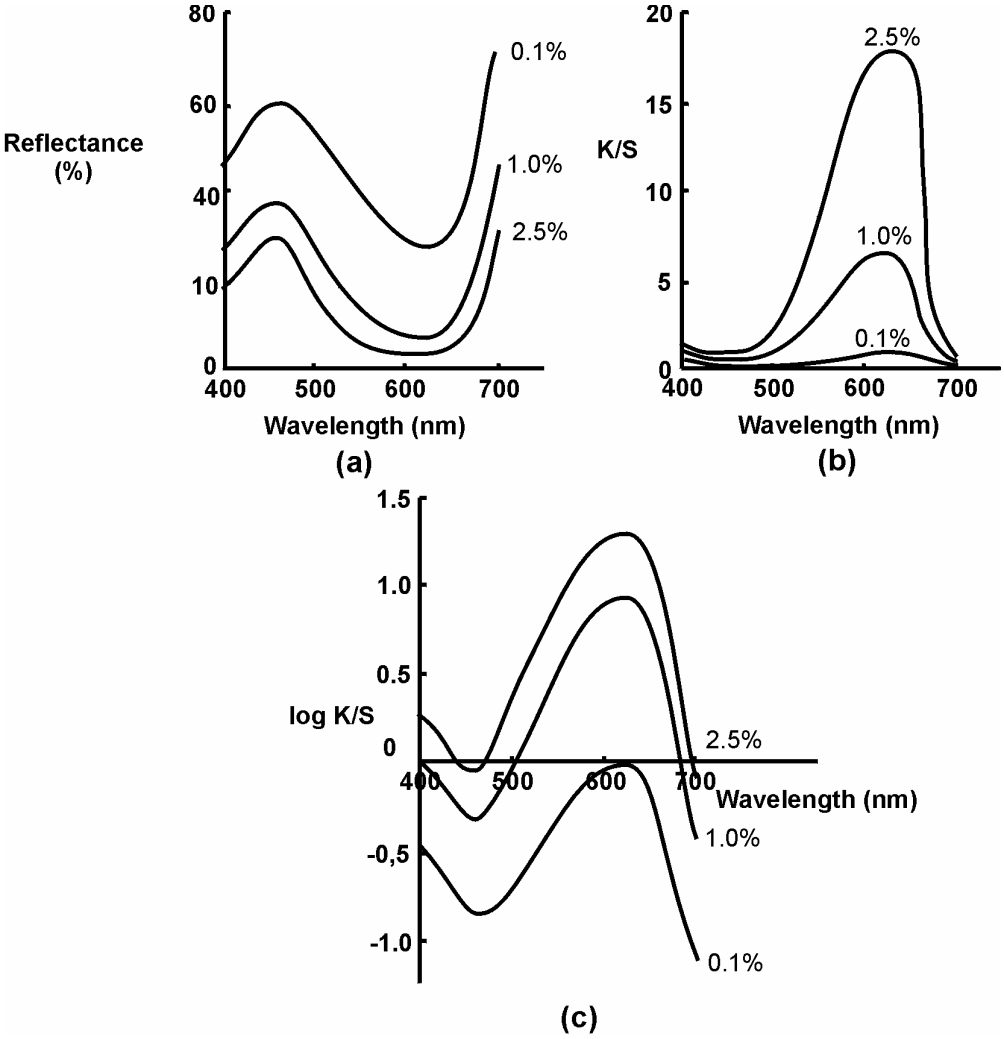

Figure 4.3 Different ways of plotting the same spectral data obtained from dyeings of Lanasyn Brilliant Blue FBL on wool at concentrations by weight of 0.1%, 1.0% and 2.5% . (a) Reflectance vs wavelength, (b) K/S vs wavelength, (c) log(K/S) vs wavelength

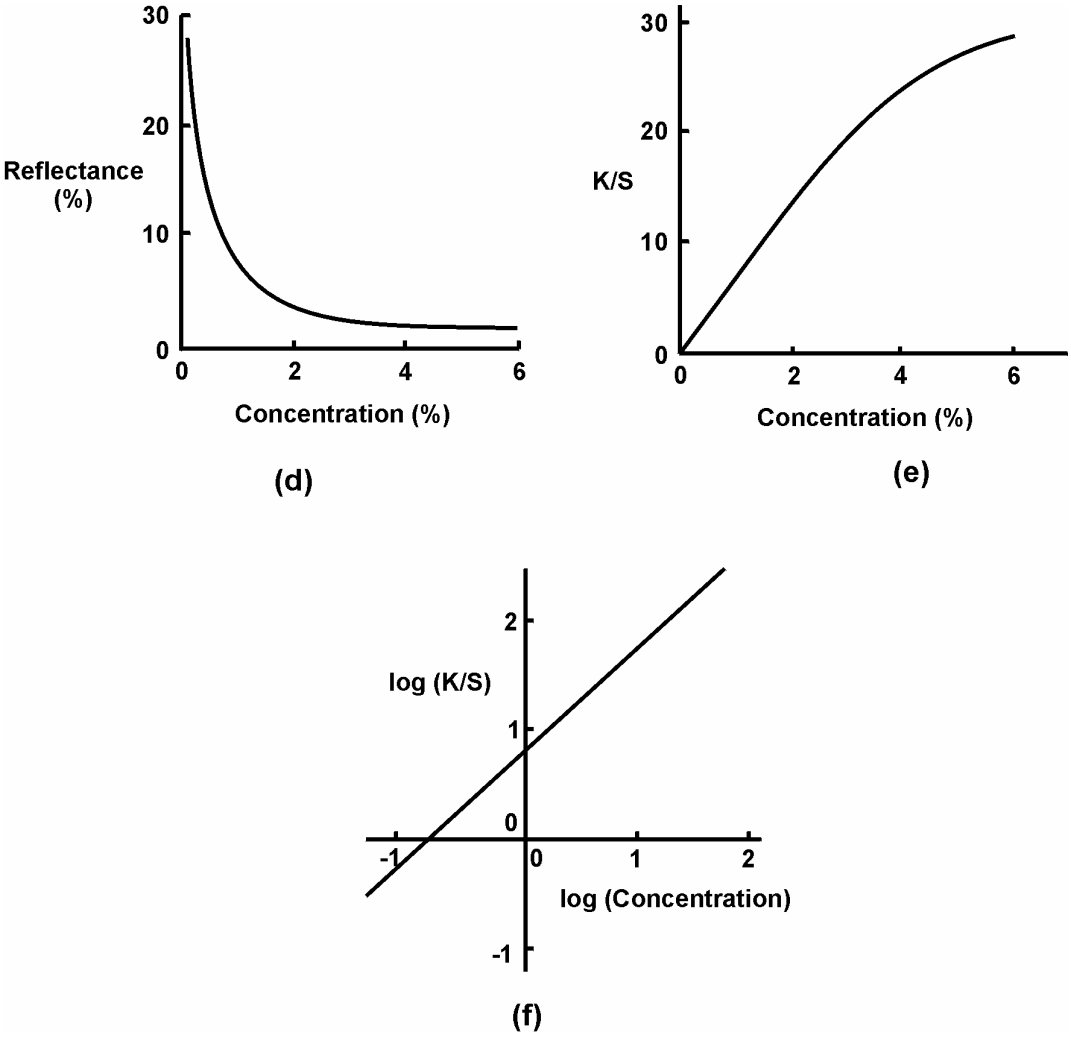

Figure 4.3 The variation in concentration with measurements at 620 nm of dyeings with Lanasyn Brilliant Blue FBL on wool, (d) reflectance values, (e) K/S values, and (f) log (K/S) vs log (concentration)

Thus by preparing calibration data from measurements of the reflectance of a series of samples of a textile substrate dyed to different depths with a particular dye, it is possible to determine the concentration of dye in an unknown sample. Apart from colour measurement, K/S values can be used in research on dye uptake as an alternative to measuring dye exhaustion in some applications.

It is important that the samples should as nearly as possible fulfil the requirements of Kubelka-Munk theory, i.e. that the fibres are evenly dyed and that the internal dyestuff concentration inside the fibres is accurately known. The dyeings should be allowed to proceed to equilibrium, the equilibrium exhaustion should be measured and the dyeings checked by cross-sectioning the fibres to ensure freedom from ring dyeing.

Recipe prediction

Recipe prediction uses reflectance data obtained from a sample as the basis for calculation of the concentrations of dyes which could be used to match the reflectance spectrum. This is most easily done with a computer specially programmed for the purpose. The general procedure will be described here.

We have already seen how Kubelka-Munk theory can be used to determine the concentration of a single dye in a textile substrate but it is also possible to extend the theory to determination of the total K/S value at any particular wavelength resulting from a mixture of dyes by a linear combination of contributions from the component dyes in a mixture:

$$(K/S)_{total} = k_1 c_1 + k_2 c_2 + k_3 c_3 + \ldots + (K/S)_S$$

where the numerical subscripts denote the component dyes in the mixture. The constant k is sometimes called a 'normalised (K/S) value' or an 'absorption coefficient'. The term $(K/S)_S$ takes into account the fact that the substrate behaves as though it is a colourant of constant concentration.

The above equation can be derived from Kubelka-Munk theory and this derivation is given in the reference for recommended reading on colour measurement.

Values for $(K/S)_S$ can be determined by measuring the reflectance spectrum of the substrate and values of k for each dyestuff can be determined at any particular wavelength, by measuring the reflectance spectra of samples dyed at a range of different concentrations.

It is usual to compute the results of a matching at a minimum of 16 wavelengths (i.e. measurements are made at 20 nm intervals between 400 nm and 700 nm), but more points can be used depending on the resolution of the reflectance spectrophotometer and the computing power available. It is rare to try to match a shade with more than four dyes and therefore, in this case, a minimum of four equations would provide a solution to the simultaneous equations. However it has been shown that at least 16 sets of data are required for reasonable accuracy. Then a large number of data sets are used, the necessary calculations are carried out using iterative algorithms and optimised dyestuff concentrations obtained. More sets of data could potentially increase accuracy but in practice it has been found there is not much advantage in doubling the number of sets. Once concentrations have been obtained, the predicted reflectance spectra, tristimulus values, L* a* b* values, and colour differences between the starting sample and predicted match can be calculated. It is claimed that the accuracy of matching can be improved by replacing the constants in the above equations by functions which relate changes in K/S with concentration to the concentration of the dye.

Colour match prediction procedure

To match a standard it is necessary to measure the spectrum of the standard to obtain the $(K/S)_{total}$ values at a minimum of 16 wavelengths and to compute the tristimulus values X_{std}, Y_{std}, Z_{std}. The sixteen equations relating K/S values to the concentrations of a set of selected dyes are then be used to compute a set of optimised concentrations c_1, c_2, c_3 etc. by solving the set of 16 simultaneous equations.

From the values of c_1, c_2, c_3 etc. it is then possible to obtain the actual predicted values of $(K/S)_{pred}$ at each wavelength and then the corresponding tristimulus values X_{pred}, Y_{pred}, Z_{pred} can be calculated for the first attempt at matching the original sample. The differences between the tristimulus values of the standard and the first prediction are then:

$$\Delta X = X_{std} - X_{pred}$$
$$\Delta Y = Y_{std} - Y_{pred}$$
$$\Delta Z = Z_{std} - Z_{pred}$$

If the values of ΔX, ΔY and ΔZ are all less than a predetermined maximum tolerance value (say 1% of X_{std}, Y_{std}, Z_{std} respectively) then the colour difference between the standard and predicted match are calculated for illuminant C $[(\Delta C)_C]$. If $(\Delta C)_C$ is less than a predetermined maximum tolerance value (say 0.5 CIE units), the degree of metamerism is calculated [say $(\Delta C)_{D65} < 2$ CIE units] and the match accepted, otherwise correction factors are calculated for the dye concentrations in an attempt to improve the match.

Colour correction

The aim of colour correction calculations is to calculate additions (or subtractions) to a starting dye recipe in an attempt to obtain an improved match using tristimulus functions.

By changing c_1, c_2, c_3 etc. each in turn by 1%, the corresponding changes in X_{pred}, Y_{pred} and Z_{pred} are calculated. The results for three dyes are expressed in the following table:

Table 4.1 Dye concentrations and corresponding tristimulus values for colour correction calculations

Sample	Dye concentrations			Tristimulus values		
Standard				X_{std}	Y_{std}	Z_{std}
Predicted	c_1	c_2	c_3	X_{pred}	Y_{pred}	Z_{pred}
Predicted	$c_1 + c_1/100$	c_2	c_3	X_1	Y_1	Z_1
Predicted	c_1	$c_2 + c_2/100$	c_3	X_2	Y_2	Z_2
Predicted	c_1	c_2	$c_3 + c_3/100$	X_3	Y_3	Z_3

A matrix is formed:

$$\begin{bmatrix} \frac{dX_1}{dc_1} & \frac{dX_2}{dc_2} & \frac{dX_3}{dc_3} \\ \frac{dY_1}{dc_1} & \frac{dY_2}{dc_2} & \frac{dY_3}{dc_3} \\ \frac{dZ_1}{dc_1} & \frac{dZ_2}{dc_2} & \frac{dZ_3}{dc_3} \end{bmatrix}$$

where $dX_1 = X_1 - X_{pred}$, $dY_1 = Y_1 - Y_{pred}$, $dZ_1 = Z_1 - Z_{pred}$ and $dc_1 = c_1/100$ etc.

The inverse of this matrix is:

$$\begin{bmatrix} \frac{\partial c_1}{\partial X_1} & \frac{\partial c_1}{\partial Y_1} & \frac{\partial c_1}{\partial Z_1} \\ \frac{\partial c_2}{\partial X_2} & \frac{\partial c_2}{\partial Y_2} & \frac{\partial c_2}{\partial Z_2} \\ \frac{\partial c_3}{\partial X_3} & \frac{\partial c_3}{\partial Y_3} & \frac{\partial c_3}{\partial Z_3} \end{bmatrix}$$

Then corrections Δc_1, Δc_2, Δc_3 to c_1, c_2, c_3 respectively are obtained by solving:

$$\begin{bmatrix} \Delta c_1 \\ \Delta c_2 \\ \Delta c_3 \end{bmatrix} = \begin{bmatrix} \frac{\partial c_1}{\partial X_1} & \frac{\partial c_1}{\partial Y_1} & \frac{\partial c_1}{\partial Z_1} \\ \frac{\partial c_2}{\partial X_2} & \frac{\partial c_2}{\partial Y_2} & \frac{\partial c_2}{\partial Z_2} \\ \frac{\partial c_3}{\partial X_3} & \frac{\partial c_3}{\partial Y_3} & \frac{\partial c_3}{\partial Z_3} \end{bmatrix} \times \begin{bmatrix} \Delta X \\ \Delta Y \\ \Delta Z \end{bmatrix}$$

$$\Delta c_1 = \frac{\partial c_1}{\partial X_1}\Delta X + \frac{\partial c_1}{\partial Y_1}\Delta Y + \frac{\partial c_1}{\partial Z_1}\Delta Z$$

Therefore the corrected value of c_1 is: $(c_1)_{corr} = c_1 + \Delta c_1$

The corrected values of c_2 and c_3 are obtained in a similar way and the corrected values of $(c_1)_{corr}$, $(c_2)_{corr}$, $(c_3)_{corr}$ etc. are then used to calculate new predicted K/S values at the 16 wavelengths and thence obtain new values of X'_{pred}, Y'_{pred} and Z'_{pred}. The procedure is repeated till the colour difference falls under the tolerance limit, or the limit set for the number of iterations to be carried out is exceeded. If a match cannot be found, the next combination of dyes is selected and the procedure is repeated for all possible the specified combinations of dyes. This procedure is illustrated in the flow chart shown in Figure 4.4.

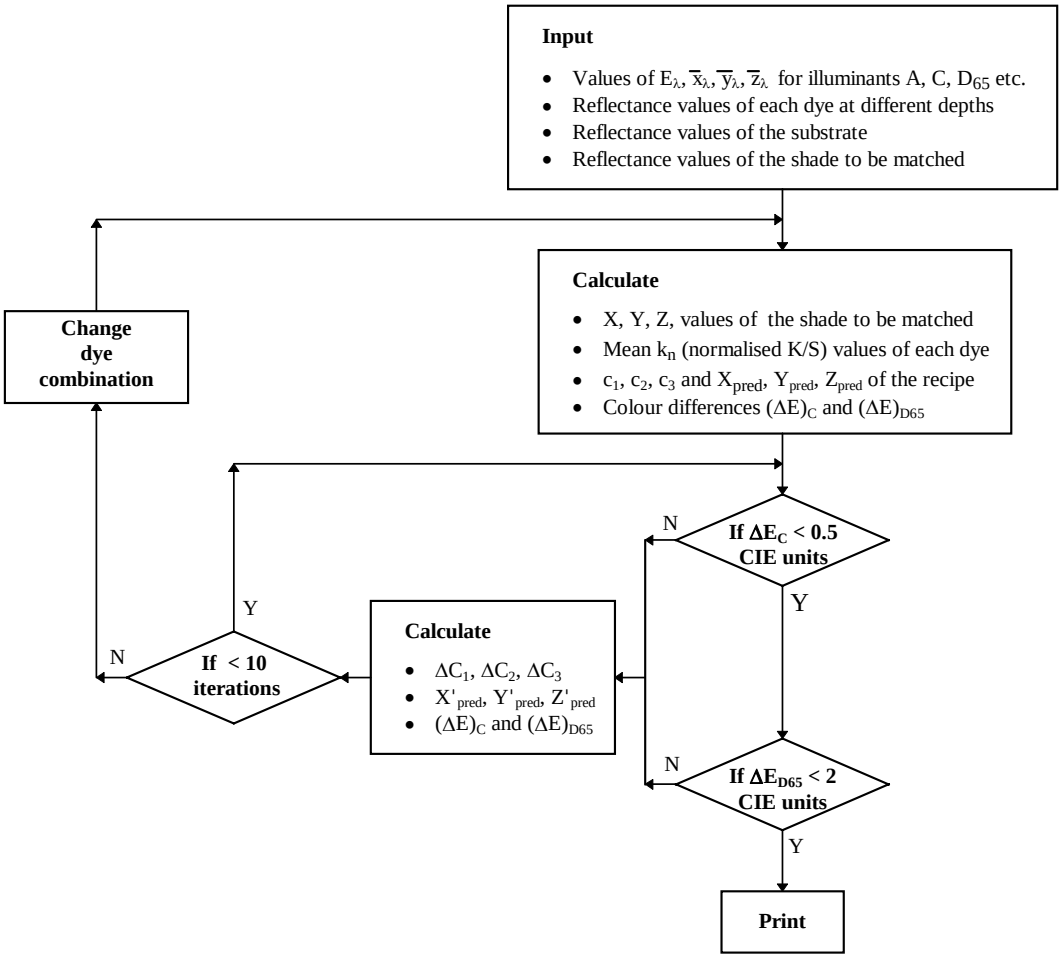

Figure 4.4 A simplified flow chart for colour recipe prediction

Practical requirements

In order to set up a practical colour matching system, it is necessary to build up an accurate data base of information. It is usual to obtain reflectance data on all the dyes of interest on the various substrates to be dyed.

It is critical that there should be good correspondence between the results of laboratory and plant dyeings. As an absolute minimum both the laboratory and large-scale machines should be under automatic control so they complete dye cycles can be reproduced accurately. Also, it is highly desirable that dispensing of all dyes and chemicals should be controlled and checked by an automated system to reduce possibilities for error.

Typically, a series of dyeings on each particular substrate must be carried out at a range of at least six concentrations varying from say 0.1% to 5% or more, depending on the dye. Dyeings should preferably be carried out in triplicate using equipment under automatic control so all the dyeing parameters can be accurately controlled. Substrates should be blank dyed using identical

procedures as the dyed samples. Multiple reflectance measurements should be made on different areas of all the samples. The accuracy of the prediction system will depend in the first instance on the accuracy of the source data. A typical set of calibration reflectance curves is shown in Figure 4.5. Current colour matching software provides matches using pre-selected combinations of dyes. A wide range of data for each match can be provided beside the predicted recipe, including colour differences between the sample and predicted match, metamerism, cost, likely fastness etc., depending on the ancillary data included in the system.

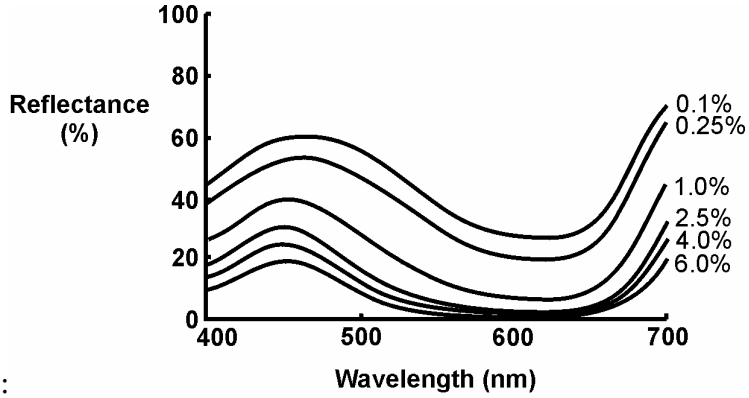

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Figure 4.5 Calibration data for Lanasyn Brilliant Blue FBL on wool top

Colour matching on blends

Recipe formulation for mixtures of fibres which require different classes of dyes, consists of predicting a recipe for each of the component fibres independently and then taking into account the relative proportions of the fibres present in the blend. The calibration data for each fibre already obtained for the pure fibre types can be used, however in practice, cross-staining of each fibre can occur and this simple approach may not work well. Developments are continuing in this area.

Blending stock-dyed fibres to produce a given colour can be the subject of computer formulation. The prediction technique is based on the assumption that the total light absorbance of the blended fibres is the sum of the component light absorbance values.

$$f(R) = af(R_1) + bf(R_2) + cf(R_3)$$

where a, b and c are the proportions of the different types of fibres present, (a + b + c = 1) and R1, R2, R3 are the reflectance values of the three individual component fibres. Also for each fibre type:

$$f(R) = \exp [- S(1 - R)^2/2R]$$

where S is an experimentally optimised scattering factor (eg. for viscose S =

0.28).

There are restrictions on the colours that can be combined if solid shade effects are to be obtained. Acceptable ranges of colours have been determined by trial and error and about 20 basic colours of dyed stock were found necessary to produce a good gamut of blended-fibre colours.

Why use instrumental colour systems?

Many case histories on the introduction of colour measurement and prediction systems in industry have been recorded. Substantial savings can be anticipated in a number of important areas.

Computer match prediction can reduce dye recipe costs by 10-30%. This is possible because recipes can be selected based on the most economical combination of dyes, either from within a dye class or from different dye classes. Combinations of dyes are often found which would not be easily discovered by manual colour matching. Dye inventories can also be reduced with decreases in overhead costs. Troublesome metameric matches can be more easily detected. Assuming a total 15% saving of dyestuff cost on an annual dye bill of $250,000, a colour matching system costing $80,000 could be paid for in about two years.

The use of a fully integrated colour matching and recipe prediction system allows the number of additions to be reduced in plant dyeings. In some cases, additions can be almost entirely eliminated. To some extent this may be assisted by the introduction of sampling machines, dyeing controllers and dosing systems which must be regarded as part of the total package. Some dyehouses report up to 96-97% of plant dyeings are “right first time”. Each addition increases the cost of a dyeing by at least 30%, not necessarily in dye cost, but in wasted machinery and operator time and in lost production. These savings may prove to be larger than economies made on dye selection and inventory and may average around a 20% reduction in total dyeing cost.

One study has shown that computer match prediction can reduce the number of trial laboratory dyeings to match a shade from 6 to 1.3. Based on an equipment cost of say $80,000, the outlay can be justified if a laboratory is required to match more than 50 shades per week.

No modern dyehouse can afford to ignore the potential savings which can result from the use of colour measurement and match prediction systems.

Review questions

1. *What precautions should be taken in selecting colour tolerance values for commercial use?*
2. *What are the causes of metamerism and which type is most troublesome to the dyer?*
3. *What are the practical requirements for reliable comparison of coloured samples?*
4. *Under what circumstances can the expense of setting up an instrumental recipe prediction system not be justified?*
5. *Under what practical conditions may it be difficult to obtain good quality recipe predictions with certain dyes?*
6. *What are the two main steps in calculation of dye recipes to match desired shades?*
7. *What are the main problems in implementing colour prediction for blends?*

Further reading

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