THE MEASUREMENT OF COLOUR

by

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PREFACE

The main purpose of this book has been to describe the principles, methods and applications of the trichromatic system of colour measurement. Not all colour measurement needs to be referred to this system, but since 1931, when the Commission Internationale de l'Éclairage adopted a set of tables which defined the colour-matching characteristics of a standard observer and established a reference framework for the specification of colours on the trichromatic system, it has become the fundamental system underlying all others. There are not many books in existence which deal with the subject, and it is my hope that the present volume will prove of some value in scientific and technical circles and among those who are anxious to know what can, and what cannot, be done in the way of measuring colour. It may also help as an introduction and guide to the great variety of original papers which are now appearing; some such foundation seems to be required, since so many of these papers are written on the assumption that the reader is already familiar with the elements of the subject.

A word should be included here about the vexed question of terminology. Two committees have been sitting during recent years to study this problem so far as it affects the English-speaking world: the first was appointed in 1933 by the Optical Society of America and sections of its report are now appearing in the Journal of that Society; the second was appointed in 1941 by the Colour Group of the Physical Society and this committee is still actively engaged on its task. I have had the privilege of knowing something of the inner workings of the American committee and of serving as a member of the English committee. I can say without any hesitation that my ideas have been greatly clarified as a result of the strenuous discussions which have taken place, and this has inevitably been reflected in the terminology in this book. At the same time I could not very well anticipate the recommendations which the Colour Group committee may propose, and I have accordingly felt it best in most cases to avoid giving formal definitions of the terms I have used. Instead, I have tried to bring out their meanings from the contexts in which they appear; this may well be the more natural method and in the present case may have the added advantage of avoiding conflict with any official definitions which may be adopted in the future.

I fear my American friends will be distressed at my use of the terms "light" and "colour", although I do not believe that we differ in any fundamental way on this issue. In particular, I have made no attempt to restrict "colour" to only one of its possible meanings, since this seemed to me an arbitrary and undesirable curtailment of the language and one not readily justifiable on the grounds of ambiguity. I should have liked to introduce the term "luminance" to replace "photometric brightness", as recommended by the American committee, but I felt this was too radical a change to be launched on this country at the whim of one individual. If such a change were to be recommended by a representative body of opinion, I should gladly fall into line. I have, however, relegated the term "primaries" to the field of subtractive colour mixture alone and I hope in consequence that this will remove at least one source of confusion between accounts of the additive and subtractive processes.

It remains for me to express my very sincere thanks to a number of people for their assistance at various stages in the preparation of this book: To Mr. F. Twyman for his encouragement and for his broad-minded policy of publishing books which are in no sense descriptions of Hilger apparatus; to Mr. J. W. Perry and Mr. T. L. Tippell, also of Hilger's, the former for his patience in reading an early and unsatisfactory draft of the manuscript and in making many suggestions for its improvement, the latter for his careful proof-reading and many helpful corrections; to Mr. R. G. Hunt of the Imperial College for reading the proofs and commenting on the text generally; to Miss Dorothy Nickerson, secretary of the Inter-Society Colour Council in the United States, for some most informative correspondence on many aspects of colorimetry but more especially in connection with the Munsell system; to Mr. R. F. Wilson and Mrs. E. M. James of the British Colour Council for information on colour atlases in general and publications of the British Colour Council in particular; to the Paint Research Station and Miss Dorothy Tilleard for the data on the bronzing of pigments illustrated in Fig. 53; and to Mr. J. M. Jack of Messrs. R. MacLehose for his expert and kindly advice about the printing of the text and the reproduction of the diagrams.

Certain of the diagrams and tables have been taken from original publications and acknowledgment is due for their reproduction: the authorship has been indicated in the text; the publishers are listed below:

The Physical Society, for Figs 56 and 57, and for tables 3, 4 and 5 in Appendix II and for the tables in Appendix III.
The Optical Society of America, for Figs. 16 and 46.
Nature, for Figs. 64 and 65.
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The University of Toronto Press, for Fig. 63.

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IMPERIAL COLLEGE OF SCIENCE,
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CONTENTS

CHAPTER I

RADIATION IN THE VISIBLE SPECTRUM: ITS EMISSION, ABSORPTION AND REFLECTION

The Nature of Light

Out of the whole gamut of electro-magnetic radiations from cosmic rays to radio waves, only a small band of radiations is capable of stimulating the eye. The limits of this band are ill-defined, since they depend on the amount of energy available, but for most practical purposes the visible spectrum may be regarded as terminating at a wavelength of $0{\cdot}40 \times 10^{-3}$ mm. on the short-wave side, and at $0{\cdot}75 \times 10^{-3}$ mm. on the long-wave side. It is true that with especially intense sources and with high aperture spectroscopes, the boundaries may be extended at least down to $0{\cdot}35 \times 10^{-3}$ mm. and even lower for some observers, and up to $0{\cdot}90 \times 10^{-3}$ mm., the limits apparently being set by absorption in the optic media at the short waves and by lack of sensitivity of the photo-chemical substances in the retina at the long waves.

Only radiations within the visible spectrum should properly be described as light radiations, in spite of the fact that there is little physical difference between these and the radiations in the ultra-violet and infra-red regions. The extraordinary importance of light to the human race lies solely in the fact that we possess in the eye a sense organ capable of reacting to light rays, yet this is a good and sufficient reason for dignifying them with a name of their own, in spite of their physical similarity to neighbouring radiations. In any case, when we refer to the measurement of light, we imply that the measurements relate to radiations in respect of their ability to stimulate the eye, hence the amount of light, as such, in the ultra-violet or infra-red region of the spectrum, is necessarily zero.

The unique physical characteristic of each radiation is its frequency of vibration; related to it, and, since the velocity *in vacuo* is the same for all radiations, inversely proportional to it, is the wavelength. The practical methods of radiating energy at different wavelengths vary very considerably from frequencies of one order to frequencies of another, as does the interaction of radiation with matter in its various forms; but these differences are rather differences in the properties of matter than of the radiations, which consist essentially of electromagnetic disturbances transmitted as displacements transverse to the direction of propagation. If the source of the radiation, or the original disturbance of the electric field, is within the nuclei of atoms, it gives rise to γ-rays having a frequency around 10^{19} per sec.; lower frequencies of 10^{17} per sec. have their origin in the inner electron shells of atoms and lead to the radiation of X-rays; light rays, frequency about 10^{15} per sec., originate in the outer electron shells, infra-red rays, 10^{13} per sec., in vibrations of atoms within the molecule and from the rotation of molecules, and so on. Generally, the smaller the dimensions of the source of the disturbance, the higher the frequency.

For the problems considered in this book, we have to note three things about the nature of light: (1) light is a form of energy radiated as a transverse harmonic vibration over a frequency range between about 4×10^{14} and $7{\cdot}5 \times 10^{14}$ per sec., or between wavelength limits roughly between $0{\cdot}75 \times 10^{-3}$ mm. and $0{\cdot}4 \times 10^{-3}$ mm.; (2) the vibrations are electro-magnetic disturbances in which the electric vector corresponds to the vibration considered in the simple harmonic theory; (3) the energy is radiated in the form of an extremely large number of elementary units of energy known as quanta, the energy in a quantum being inversely proportional to the wavelength of the light radiated.

The difficulties which have existed in understanding how wave and particle properties can be harmonised in a comprehensive theory of light, need not concern us here. We make use of both aspects from time to time in colorimetry: the quantum theory provides the theoretical basis for determining the energy distribution in the radiation from a black body heated to some given temperature, it is involved in relating the spectral sensitivity of the retina to the absorption curve of the photo-chemical substances isolated from the retina, and chemists have to make use of it when analysing the absorption that occurs in a dye or pigment; on the other hand, calculations such as the loss of light by reflection in terms of the refractive index of the medium at which the reflection takes place, are made with the aid of the electro-magnetic wave theory. For the great majority of problems in colorimetry, however, light has only to be regarded, physically, as various amounts of energy radiated at various frequencies within the visible spectrum and propagated as transverse vibrations at a very high velocity. The physical identification of the different parts of the spectrum may be secured either by the appropriate frequency or the corresponding wavelength. Frequency is the characteristic which is independent of the medium within which the light is travelling, but wavelengths can be measured with greater absolute accuracy (since they do not depend for their determination on a knowledge of the velocity of light). The so-called " wave-number ", which is defined as the number of waves per centimetre, is proportional to the frequency yet does not suffer from its numerical uncertainty, but since wavelength scales have been so extensively used in colorimetric literature, and wavelength values have become so intimately associated with particular spectral lines and with the different parts of the spectrum, the time seems to have passed when they could have been conveniently displaced by the corresponding wave-numbers. As a consequence, the more familiar wavelengths (symbol λ) are retained in this book.

Light has other properties apart from its power to affect the eye. When it strikes the surface of an object, some fraction of the incident energy is generally absorbed and, if the surface is black and matt, the fraction will be large. The effect of the absorbed light is to heat the body. Again, light serves as the agent of numerous photo-chemical reactions, including the reaction which takes place in the retina, and in particular can be recorded by the many types of photographic emulsions which are now available. Light can be converted into electrical energy by photo-electric action. This may take one of three forms: (1) in the photo-emissive cell electrons are emitted from a suitably prepared surface of one of the alkali metals, *e.g.* potassium or cæsium, under the impact of a beam of light and the action of an applied potential; (2) light may cause a change in the resistance of certain materials, notably selenium, and thus lead to a change in the flow of a current through a closed circuit in which a suitably designed cell, such as a selenium cell, forms one of the components; (3) in the barrier layer type of photo-cell light falls on a surface such as cuprous oxide on copper, which possesses rectifier properties, and produces a potential difference sufficient to cause a small current to flow in a low resistance circuit in which there is no other source of potential. Indirectly, light can be converted into electrical energy by focussing it on to the junction of two metals such as constantan and manganin, at which a potential is developed when the temperature is raised. Finally, light may be absorbed by certain crystals, such as activated zinc sulphide, and other chemical substances, and part of the energy be re-radiated as light of a longer wavelength. This phenomenon, known as fluorescence, is chiefly of interest in colorimetry when the incident radiation or stimulus comes from the violet or ultra-violet region of the spectrum, in which case much of the re-radiation occurs in the visible spectrum.

Light Sources

The most common method of making a body emit light is to heat it. As the temperature rises, the activity of the atoms and molecules in the substance greatly increases; their impacts become more frequent and more violent and the resulting electro-magnetic radiations increase in strength and spread to shorter and shorter wavelengths. Thus the traditional poker when heated in a fire at first radiates heat but no light.

As it gets hotter, it begins to glow a dull red, then a bright red, gradually becoming brighter and whiter as more energy, both relatively and absolutely, is radiated in the green and blue parts of the spectrum.

A few experiments suffice to show that the distribution of energy through the spectrum is a function principally of the temperature of the body rather than of the material of which it is composed. When a perfectly black body, that is to say, a body that completely absorbs all the energy in a beam of light illuminating it, is heated, it can be shown from considerations of thermal equilibrium that the energy radiated per unit area of its surface has a definite magnitude and a definite distribution through the spectrum depending only on its temperature. A typical curve for a black-body radiator is shown in Fig. 1.

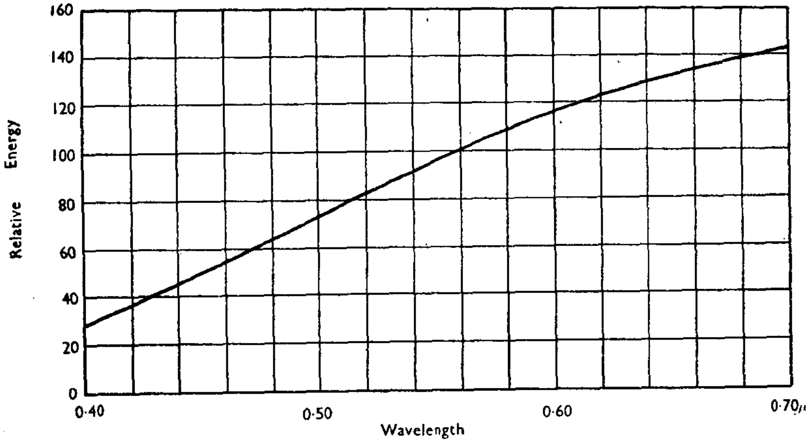

Fig. 1. The energy distribution curve for a black-body radiator heated to a temperature of 3500° K.

A close approach to a black body is not easily obtained, since most surfaces reflect some light and many show a certain amount of selective absorption, as indicated by their colour. This results, when such bodies are heated, in a departure from a true "black-body" distribution of energy, although at no wavelength will the radiation of energy exceed that given by a black body heated to the same temperature. With some materials, for example tungsten, the colour of the light from the substance at one temperature can be matched by the colour of the light from a black body heated to a different temperature, in which case the energy distribution of the source can be defined by reference to the matching temperature of the black body. This temperature is known as the colour temperature and may be either higher or lower than the true temperature of the heated material, according as the latter tends to radiate relatively more or less light at the blue end of the spectrum. The energy distribution need not be, and is indeed unlikely to be, identical to that of the black body at the stated colour temperature, since, as will be evident from later chapters, it is quite possible for two beams of light to give rise to the same colour sensation while possessing very different energy distributions. With materials such as tungsten, however, in which the selective absorption is not marked, the deviations from the black-body distribution are small and may in many cases be ignored.

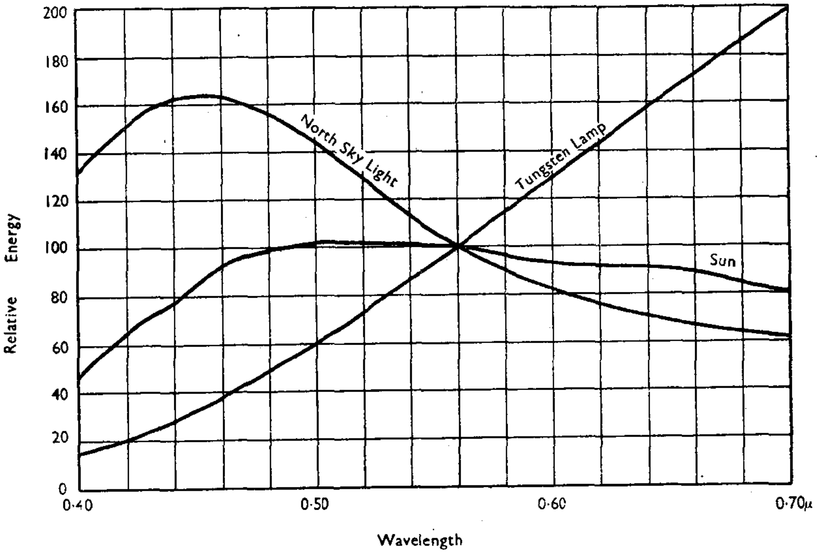

FIG. 2. Energy distribution curves for a gas-filled tungsten lamp, the sun and north sky light.

The energy curves for three common sources of light, a gas-filled electric lamp, the sun and north sky light, are shown in Fig. 2. All three are generally similar to black-body radiators, the lamp having a colour temperature of the order of 2900° K (K stands for the absolute or Kelvin temperature scale), but varying according to the voltage applied, the sun a colour temperature around 5000° K but subject to variations due to atmospheric absorption, altitude, and so on, and the north sky being considerably bluer with a colour temperature of the order of 15,000° K or higher. The north sky light is the least capable of exact definition, since it varies widely according to the amount of cloud, the place at which measurements are made, the atmospheric pollution, the time of day, the time of year, and so forth.

North sky light has been widely used in the past as an illuminant to compare coloured samples, but on account of its variability there has been a demand for an artificial illuminant of similar but constant quality. A reasonable approximation to daylight of almost any colour temperature can now be secured by means of a tungsten filament lamp run at a specified colour temperature in conjunction with liquid colour filters of specified chemical composition and thickness.* A standard illuminant is therefore only a matter of national and international agreement, a goal which was achieved in 1931 by the Commission Internationale de l'Éclairage. Unfortunately, complete unanimity about the average quality of daylight could not be secured, the United States preferring a colour temperature of 6500° K as more representative of their conditions, while Great Britain considered 4800° K to be a better approximation to the conditions there. As a result, two sources known as S_B and S_C were defined as two alternatives to daylight, to be used according to the preference of the individual. The colour temperatures of S_B and S_C are respectively 4800° K and 6500° K, but more recently suggestions have been made in the United States that a higher colour temperature would be a truer representation of daylight. In view of the wide variability of daylight, the advantages of one illuminant over another are not very apparent; the important point is to secure uniformity of practice and from this aspect the standardisation of both S_B and S_C is to be regretted. Since 1931, filters have been designed by means of which an approximation to an equal-energy distribution can be produced; by this is meant a distribution in which the energy radiated within unit waveband $\Delta\lambda$ at wavelength λ within the visible spectrum, is the same for all values of λ. An equal-energy source, which may be referred to as S_E, might be considered as a substitute both for S_B and S_C and some discussions to this effect have already taken place. Its general use would avoid the divergence of practice now prevalent, and, as will appear from later chapters, the standard system of colour specification, which centres around the equal-energy source, would have its logical counterpart in practical measurement. An additional source, known as S_A, has also been defined to provide an illuminant to correspond to average artificial lighting. In many instances, coloured materials and surfaces are seen primarily in artificial light, so that a colour specification measured with the sample illuminated by daylight would be in error by an important amount. A standard artificial illuminant is therefore required and the need is met by S_A, which consists of a tungsten lamp run at a colour temperature of 2848° K. The details regarding S_A, S_B, S_C and S_E are given in Appendix I, but it must be appreciated that only the first three possess international status and, as the table of energy values

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* R. Davis and K. S. Gibson, *Bur. Stand., Misc. Pub.* No. 114, 1931; and *Bur. Stand. Res. Paper* No. 652; *J. Research*, **12**, 263, 1934.

shows, the S_E source described does not possess an exact equal-energy distribution, even though its overall colour is identical to a true equal-energy source.

There are, of course, many sources of light other than those already mentioned, and in special problems the particular qualities of the illuminant may have to be taken into account. Flame sources, such as the candle or the oil lamp, are yellow in colour, the gas jet and acetylene flame are whiter, and the incandescent gas mantle gives a bright, white light, although the energy distribution departs somewhat from a black-body distribution. The carbon arc, again, provides a very intense white source.*

All these sources produce their radiation by heat, caused either by the passage of electricity or by combustion. Light can also be obtained by electric discharge through gases, as in the mercury lamp, where the disturbances leading to the radiation of energy originate in the collision of ions of the gas during the passage of the current through the gas. Under these conditions, radiation usually occurs only at isolated points through the spectrum, at the frequencies characteristic of the gas being excited. Gas discharge lamps are of great value in the laboratory as sources of monochromatic light and in the calibration of a spectrum scale in wavelengths. They have, however, little use as illuminants for colorimetry, although the colouring properties of the mercury arc and the sodium lamp may have to be borne in mind, since these lamps are employed in street lighting installations and elsewhere.

A development of the gas discharge lamp into an illuminant of very wide application has been achieved by making use of fluoresecent powders that re-radiate in the visible spectrum when excited by ultra-violet radiations. Thus, in the most important form of lamp, the inner glass wall of a mercury discharge tube is lined with a suitable mixture of fluorescent powders and excited by the strong ultra-violet radiation which is present in the mercury spectrum. The light radiated by the lamp as a whole is a combination of the light from the fluorescent powders and that from the mercury lines in the visible spectrum; by a proper choice of powders a close approximation to the colour of daylight can be secured, although it does not necessarily follow that the energy distribution is an equally close approximation to a black-body distribution. These lamps have already been widely employed in industry and are likely to find many uses in other spheres, not only in their daylight form but also in warmer colours. They may well prove of value as illuminants in the colour industries and in colorimetry, but it is certain that their colour-rendering characteristics will have to be

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* Further details such as the brightness, colour temperature, etc., of these and other sources can be obtained from any standard text-book on photometry, *e.g.* *Photometry*, by J. W. T. Walsh (Constable), 1926.

allowed for when they are adopted for decorative and domestic schemes of lighting.

Fluorescence also occurs when fluorescent powders are bombarded with a beam of electrons, as in the cathode ray tube, or by activating fluorescent materials with radio-active compounds, although there is no evidence that these methods are at present likely to lead to the development of practical light sources of any consequence in colorimetry. On the other hand, the use of fluorescent dyes and pigments, particularly for producing enhanced decorative effects, is likely to provide new and interesting problems of colour measurement.

The Measurement of Energy Distribution

The measurement of relative energy radiated at various wavelengths through the spectrum by a given light source is no easy matter if the results are not to be obtained by comparison with a source whose energy distribution is known or can be assumed. The eye cannot be used for absolute measurements of energy, since its sensitivity varies with wavelength, and this is also true for the different types of photo-electric cell. The thermopile is the only device in which the response is a function of energy alone, independent of wavelength, since a properly blackened thermo-junction absorbs light equally from all parts of the spectrum. Compared with the photo-cell, the thermopile is very insensitive, and reliable energy measurements require the use of very sensitive galvanometers with many precautions to avoid spurious results. Fortunately, investigations carried out at the larger research laboratories and institutions have established the distribution of energy from black-body radiators and other sources, and an unknown energy distribution can now be determined by reference to sources calibrated against these absolute measurements. Tungsten lamps operating at a specified colour temperature form a very convenient sub-standard of energy distribution.

When a known and an unknown energy distribution are to be compared, the essential observation consists merely in a comparison of the energies in the two beams at a number of wavelengths through the spectrum. Since at any wavelength the two beams, being monochromatic, have identical energy distributions, the comparison is independent of the spectral sensitivity of the light detector, whether eye or photo-cell, and the measurements, while still calling for many refinements, are no longer of the exacting kind associated with absolute determinations.

The Absorption of Light

When a beam of light, as represented by the arrows in Fig. 3, is travelling through a medium, a certain amount of energy may be lost owing to absorption or scattering. If the light travels a distance l in the medium in going from A to B, and if the energy or intensity is represented by I_0 when the beam is at A and by I when it has arrived at B, then I will be less than I_0 by an amount depending on the distance l and on the degree of scattering and absorption occurring in the medium. If the medium is very clear and colourless, I will be effectively equal to I_0 but in all other cases it will be reduced. The reduction due to the scattering depends on the size of the particles producing the scattering relative to the wavelength of light, on their shape, on the refractive index relative to that of the surrounding medium and so on. Exact analysis is often impossible, so that particular problems may have to be solved empirically or by making reasonable approximations.

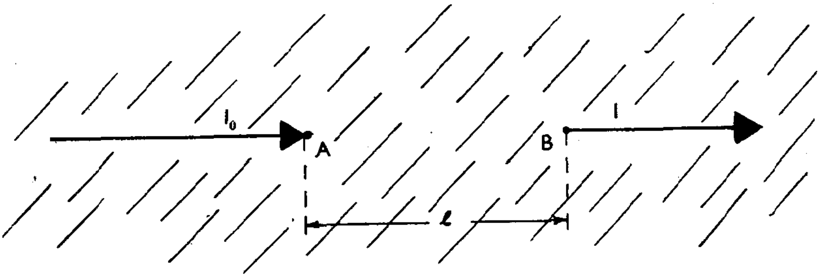

FIG. 3.

The loss of light by absorption alone can be evaluated without difficulty once certain constants of the absorbing medium are available, although its interpretation in terms of the structure and nature of the medium is still a matter of great intricacy. Generally, it may be said that absorption of light of any given frequency occurs through resonance between the light frequency and some part of the molecule which possesses a corresponding period of vibration. In vapours and gases at low pressures, the resonators can be regarded as being very sharply tuned to particular frequencies and consequently absorb only at those frequencies in the spectrum. The absorption spectrum under these conditions may therefore appear as discrete lines, or as very fine lines packed very close together. At increased pressures, and even more in the case of liquids and solids, the close proximity of neighbouring molecules exerts a disturbing influence which tends to blur out the sharp resonance that would otherwise exist. The spectrum then shows broad absorption bands in which different wavelengths are absorbed in greater or less degree according to the nature of the molecular structure. It is extremely difficult to predict the character of the absorption bands in a complex molecule, except in those cases where the resonators are independent and shielded from one another. Where some degree of