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COMMISSION INTERNATIONALE DE L'ECLAIRAGE
INTERNATIONAL COMMISSION ON ILLUMINATION
INTERNATIONALE BELEUCHTUNGSKOMMISSION

TECHNICAL REPORT

CALIBRATION METHODS AND PHOTO- LUMINESCENT STANDARDS FOR TOTAL RADIANCE FACTOR MEASUREMENTS

CIE 182:2007

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Radiance

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5. De maintenir une liaison et une collaboration technique avec les autres organisations internationales concernées par des sujets relatifs à la science, la technologie, la normalisation et l'art dans les domaines de la lumière et de l'éclairage.

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3. Richtlinien für die Anwendung von Prinzipien und Vorgängen in der Entwicklung internationaler und nationaler Normen auf dem Gebiet der Lichttechnik zu erstellen.
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This Technical Report has been prepared by CIE Technical Committee 2-25 of Division 2 Physical Measurement of Light and Radiation and has been approved by the Board of Administration of the Commission Internationale de l'Eclairage for study and application. The document reports on current knowledge and experience within the specific field of light and lighting described, and is intended to be used by the CIE membership and other interested parties. It should be noted, however, that the status of this document is advisory and not mandatory. The latest CIE proceedings or CIE NEWS should be consulted regarding possible subsequent amendments.

Ce rapport technique a été élaboré par le Comité Technique CIE 2-25 de la Division 2 Mesures physiques de la lumière et des radiations et a été approuvé par le Bureau de la Commission Internationale de l'Eclairage, pour étude et emploi. Le document expose les connaissances et l'expérience actuelles dans le domaine particulier de la lumière et de l'éclairage décrit ici. Il est destiné à être utilisé par les membres de la CIE et par tous les intéressés. Il faut cependant noter que ce document est indicatif et non obligatoire. Il faut consulter les plus récents comptes rendus de la CIE, ou le CIE NEWS, en ce qui concerne des amendements nouveaux éventuels.

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CALIBRATION METHODS AND PHOTOLUMINESCENT STANDARDS FOR TOTAL RADIANCE FACTOR MEASUREMENTS

SUMMARY

This technical report provides the recommendations of the CIE concerning total radiance factor measurements of photoluminescent samples. The scope is limited here to photoluminescent samples whose fluorescence is excited by ultraviolet or visible radiation only. These recommendations include procedures for both one-monochromator and two-monochromator methods. Detailed information is provided on the influence of various measurement parameters, such as the illuminant, instrument geometry, polarization, reflectance standard and photoluminescent standard. The report includes a survey of currently available photoluminescent material standards and calibration laboratories.

METHODES D'ETALONNAGE ET ETALONS DE PHOTOLUMINESCENCE POUR LES MESURES DU FACTEUR DE LUMINANCE ÉNERGÉTIQUE TOTALE

RESUME

Ce rapport technique donne les recommandations de la CIE concernant les mesures du facteur de luminance énergétique totale pour des échantillons photoluminescents. On se limite ici à des échantillons photoluminescents dont la fluorescence est excitée seulement par de la radiation ultraviolette ou visible. Ces recommandations incluent les procédures pour les méthodes utilisant soit un monochromateur ou deux monochromateurs. De l'information détaillée est donnée sur l'influence de différents paramètres de mesure, comme par exemple l'illuminant utilisé, la géométrie de l'instrument, la polarisation, et les étalons du facteur de réflexion et de photoluminescence utilisés. Le rapport inclut un relevé des matériaux présentement disponibles comme étalons de photoluminescence et un relevé des laboratoires d'étalonnage.

KALIBRIERVERFAHREN UND LUMINESZENZNORMALE FÜR MESSUNGEN VON GESAMTSTRAHLDICHTFAKTOREN

ZUSAMMENFASSUNG

Dieser technische Bericht enthält die Empfehlungen der CIE für die Messung des Gesamtstrahldichtefaktors von Lumineszenzproben. Der Anwendungsbereich ist hier auf fotolumineszierende Materialien begrenzt, deren Fluoreszenz nur durch ultraviolette oder sichtbare Strahlung angeregt wird. Die Empfehlungen beziehen sich auch auf Verfahren, die einen oder zwei Monochromatoren verwenden. Genauere Informationen über die verschiedenen Einflüsse auf die Messung, sowie Beleuchtung, Aufbau des Instruments, Polarisation, Reflexionsgrad und Lumineszenz sind angegeben. Die Arbeit gibt einen Überblick von zur Zeit erhältlichen Lumineszenznormalen und über Laboratorien, die mit Kalibrierungen beauftragt sind.

1. INTRODUCTION

In recent years, there has been an increasing use of fluorescent colorants and whitening agents in the manufacture of paints, plastics, papers, and textiles for a diverse range of applications. These applications include enhanced visibility of safety and security goods, increased detection in process monitoring, and apparent enhancement in whiteness and brightness to improve the appearance of a variety of consumer goods. This has, in turn, increased the demand for reference standards and procedures for accurately predicting the colour appearance of these fluorescent materials when irradiated under specified conditions of daylight or artificial illumination.

An evaluation of one-monochromator methods for predicting colorimetric properties of luminescent materials under standard illuminants, was carried out by a task force on colorimetric aspects of luminescence within CIE Technical Committee TC 2.3 on Photometric Characteristics of Materials and by CIE Technical Committee TC 2-08 on Luminescence Intercomparisons, both chaired by F.W. Billmeyer, Jr. [1]. Between 1979 and 1983, TC 2-08 conducted an intercomparison of measurements of the total spectral radiance factor of luminescent materials [1]. The intercomparison involved seven luminescent specimens and four laboratories. The measurements were performed with direct specimen illumination under a source simulating D65, using either a bidirectional or sphere geometry. The raw measured total radiance factor data were mathematically corrected to irradiation by D65. These results were reported in the literature in 1988 and indicated a relatively poor state-of-the-art for these measurements [2]. The colour differences from the reference laboratory values ranged from 3,0 to 4,2 CIELAB units over all data sets and specimens.

The two-monochromator method, which involves monochromatic irradiation and monochromatic measurement, provides the most accurate method for the determination of total spectral radiance factors of luminescent materials. However, the instrumentation is complex, the measurement procedures are lengthy, and the calculations are complex. In practice, the two monochromator method is not well understood and until 1998 was carried out by only a few standardizing laboratories. More recently, instruments for measuring fluorescent materials based on the two monochromator method have become commercially available and it is expected that this will increase the industrial applications of fluorescent colorimetry.

Because of this situation, a new CIE Technical Committee (TC 2-25) was formed in 1990 to review the state-of-the-art practices for colour measurements of photoluminescent materials. The purpose of this technical report is to provide information on the principles and procedures for measuring accurately total radiance factors of photoluminescent materials by both the one- and two-monochromator methods. The report also intends to discuss the most important problems in standardization due to the use of different instrument designs, different daylight-simulating sources, and different photoluminescent and reflectance standards. Recommended procedures are given for reducing the influence of these various parameters to achieve good inter-instrument agreement and accurate colorimetric results. It is also hoped that this report will help identify areas where improved measurement methods and instrumentation are required.

1.1 Definition of problem

Colour measurements of non-photoluminescent materials are fairly straightforward since the reflected or transmitted radiation is of the same wavelength as that incident on the sample. A simple ratio measurement of these radiant fluxes gives directly the reflected or transmitted radiance factor at the wavelength of incidence. This quantity is independent of the particular instrument source used provided that it has sufficient energy over the visible range. These measurements are typically made with a conventional spectrophotometer in monochromatic or polychromatic mode where the monochromator precedes or follows the sample, respectively, and the reflected or transmitted flux is analyzed.

However, for a photoluminescent material, the colour appearance depends upon the combined effect of the fluoresced and reflected radiation, where the radiation emitted by fluorescence has a range of lower energy (longer wavelengths) than the exciting radiation. A simple ratio measurement of the emitted to the absorbed radiation is not valid since the

wavelength of the respective radiations is not the same. To determine the fraction of fluoresced radiation, it is necessary to integrate the number of photons appearing as fluoresced radiation over the entire fluorescence band and ratio this to the number of photons in the incident radiation. This is known as the fluorescent quantum yield or efficiency. For a non-fluorescent material, the quantum yield is simply the conventional reflected or transmitted radiance factor.

The intensity of fluoresced radiation at a particular wavelength λ depends upon: (1) the spectral quantum efficiency of the fluorescent process, $\eta_L(\lambda)$ and (2) the total number of incident photons that are capable of exciting fluorescence, N . The luminescent radiance factor, which measures the ratio of this radiance due to photoluminescence to that reflected from the perfectly reflecting diffuser, therefore depends upon the relative amount of source energy available in the excitation region to the efficiency in the emission region, i.e. the relative spectral power distribution of the light source used. For colour measurements of photoluminescent materials to agree with visual assessments, it is therefore necessary to: (1) irradiate the specimen with an instrument source which accurately simulates the specified standard illuminant and measure the combined reflected and fluoresced radiation monochromatically or; (2) irradiate the specimen with monochromatic radiation and measure the reflected and fluoresced radiation separately and compute the total spectral radiance factor for the specified standard illuminant. The first of these procedures involves the one-monochromator method and the second of these procedures involves the two-monochromator method.

The following discussion will describe the instrumental requirements and standardization procedures concerned with both the one- and two-monochromator methods. It provides information on the influence of illuminant, instrument geometry, instrument polarization, reflectance standard and luminescent standard on achieving accurate colorimetric results. Recommendations are given for standardizing procedures to improve inter-instrument agreement. The report also includes a survey of currently available photoluminescent material standards and a bibliography of related documentary test methods.

1.2 Terminology

The terminology for describing colorimetric measurements of photoluminescent materials is defined below and follows closely that recommended in the field [3-6].

luminescence

emission of optical radiation caused by any non-thermal process

fluorescence

emission of optical radiation (light) when a substance is exposed to any type of electromagnetic radiation, where the emitted radiation appears within 1 ns to 100 ns after the excitation. This is due to a direct transition from the photo-excited energy level to a lower level.

NOTE In organic substances, this is due to an “allowed” transition generally from an excited singlet state to the ground singlet state.

fluorescence emission coefficient $F(\lambda)$

fluorescence emitted by the sample per unit wavelength interval ($\Delta\lambda$) and per unit excitation energy of the excitation wavelength μ

phosphorescence (ILV 845-04-23)

any delayed emission of optical radiation which appears more than 100 ns after the excitation. This delay is due to the storage of energy at an intermediate energy level.

NOTE In organic substances, this delayed emission is due to a “forbidden” transition generally from an excited triplet state to the ground singlet state.

photoluminescence

luminescence caused by absorption of optical radiation

NOTE 1 For the purposes of this document, photoluminescence refers to luminescence induced by absorption of visible and/or UV radiation only.

NOTE 2 The operational definition of photoluminescence is luminescence that has lifetimes shorter than the time constants of the detection system. Thus, for radiometric and colorimetric characterization, photoluminescence cannot be distinguished from fluorescence and the two terms are used interchangeably in this document.

radiance factor, β (at a surface element of a non-self-radiating medium, in a given direction, under specified conditions of irradiation)

ratio of the radiance of the surface element in the given direction to that of the perfect reflecting or transmitting diffuser identically irradiated

Unit: 1

NOTE 1 For photoluminescent media, the radiance factor contains two components, the **reflected radiance factor, β_R** and the **luminescent radiance factor, β_L** . The sum of the reflected and luminescent radiance factors is the **total radiance factor, β_T** :

$$\beta_T = \beta_R + \beta_L$$

NOTE 2 The subscript R is used here because it is more intuitive than the traditional S and avoids confusion with the use of S to denote a state of polarization.

bispectral luminescent radiance factor, $\beta_{L\lambda}(\mu)$

ratio of the radiance per unit emission bandpass $d\lambda$ (1 nm) at wavelength λ , due to photoluminescence from the specimen when irradiated at wavelength μ to the radiance of the perfect reflecting diffuser identically irradiated and measured

Unit: nm^{-1}

NOTE 1 For spectral quantities with a subscript λ in their designation indicate differential spectral radiometric quantities. These specify the concentration of the radiometric quantity in a 1 nm interval at the specified wavelength λ .

NOTE 2 When the bispectral luminescent radiance factor is integrated or summed over an emission spectral width ($\Delta = \lambda_{\max} - \lambda_{\min}$), this quantity becomes the **weighted bispectral luminescent radiance factor, $\beta_{L\lambda}(\mu) \cdot \Delta$** .

NOTE 3 The tabular form of complete bispectral luminescent radiance factor or weighted bispectral luminescent radiance factor and reflected radiance factor data is the Donaldson matrix representation of bispectral radiance factor, $D(\mu, \lambda)$ [43]. The excitation wavelengths μ are tabulated in the vertical direction, the emission wavelengths λ in the horizontal direction, the reflected radiance factors $\beta_R(\lambda)$ appear on the diagonal where the excitation and emission (detection) wavelengths are equal, $\mu = \lambda$, and the array of weighted bispectral luminescent radiance factor data, $\beta_{L\lambda}(\mu) \cdot \Delta$ appear on the off-diagonal.

fluorescent radiant efficiency

ratio of the radiant power emitted by fluorescence for a given spectral excitation, to the spectral radiant excitation power irradiating the fluorescent material

NOTE In fluorescence colorimetry, the reference spectral radiance excitation power irradiating the sample is measured using a diffuse reflectance standard and the measured efficiency is the external fluorescent radiant efficiency unless the data have been further corrected for errors due to the sample itself, such as refraction at the sample boundaries and artifacts due to the experimental conditions (e.g. instrument geometry used). In this latter case, the corrected efficiency is the internal fluorescent radiant efficiency.

spectral quantum efficiency of the fluorescent process, $\eta_L(\mu)$

ratio of the total number of photons of all wavelengths emitted from the specimen by the fluorescent process for an excitation at wavelength μ to the number of photons at wavelength μ reflected from the perfectly reflecting diffuser identically irradiated and viewed

Unit: 1

total photon excitation, N

total number of photons irradiating the specimen that are capable of exciting fluorescence

relative spectral distribution of radiance due to fluorescence, $F(\lambda)$

ratio of the spectral distribution of radiance due to fluorescence to the sum of the tabulated values of this distribution, i.e. $\sum_{\lambda} F(\lambda) = 1,0$

luminance factor, β_v (at a surface of a non-self-radiating medium in a given direction, under specified conditions of illumination)

ratio of the luminance of the surface element, in the given direction to that of the perfect reflecting or transmitting diffuser identically irradiated and measured

Unit: 1

NOTE 1 For photoluminescent media, the luminance factor contains two components: the **reflected luminance factor**, $\beta_{v,R}$ – and the **luminescent luminance factor**, $\beta_{v,L}$. The sum of the reflected and luminescent radiance factors is the **total luminance factor**, $\beta_{v,T}$:

$$\beta_{v,T} = \beta_{v,R} + \beta_{v,L}$$

NOTE 2 The subscript R is used here because it is more intuitive than the traditional S and avoids confusion with the use of S to denote a state of polarization.

monochromatic mode

spectrophotometric mode of measurement, where the means of wavelength separation (monochromator, bandpass filters/wedge) precedes the sample and the total (reflected or transmitted plus fluoresced) radiant flux leaving the specimen is measured by the detector at the stated monochromatic wavelength

polychromatic mode

spectrophotometric mode of measurement where the specimen is irradiated by undispersed light and the total (reflected or transmitted plus fluoresced) radiant flux leaving the specimen is measured wavelength by wavelength by the detector

2. BACKGROUND**2.1 Fluorescent whitening agents (FWAs) in textiles and paper****2.1.1 Whitening: industrial significance**

The production of white goods has been a matter of special interest in many industrial processes. One of the main activities of the textile industry has been looking for methods and processes to increase the whiteness of clothing starting with the process known as bleaching. The flat-cleaving activity of alkaline ash was used as a first form of detergent with bleaching effect in an attempt to clean and brighten clothes made from linen and its relatives. Later lime, as found in nature, was applied as an effective bleaching agent. Ancient Rome used sulphur dioxide and the more readily available uric acid found in urine. Urine bleaching persisted up to the 19th century because of its mild action.

Chemical bleaching started toward the end of the 18th century when chlorine bleaching was introduced. Its action is based on the chemical destruction of coloured impurities in the cloth and is far more effective than any other method used previously. It is so effective that a prolonged treatment can damage the cloth and its use must be limited using controlled conditions. Initially, chlorine bleaching was achieved by directly applying chlorine gas. Beginning in the 1920s sodium hypochlorite, sodium sulphite and hydrogen peroxide were used. In the late 1930s, sodium chlorite was introduced. The quest for simpler and milder chemical bleaches for household use continues into modern times, with sodium perborate being the most widely used chemical bleach in modern detergents. The process has evolved into the development of a method to transform the natural off-white appearance of cotton and other cellulose derivatives into a good white. Chemical bleaching achieved this goal by destroying impurities, modifying chemically the surface of the substrate. A first physical method to increase whiteness came from the observation by dyers that off-white textiles could be made to look whiter by tinting them with blue dyes. In fact, blueing just compensates the reflected yellow light with small amounts of the complementary colour blue – resulting in a substrate perceived by the eye as a better white. It must be kept in mind that the addition of a dye causes absorption of light and as such the process results in losses of reflected light; the perceived white is less brilliant and duller. A possible problem involved in blueing or tinting is the change of the shade of the resulting white depending on the nature of the substance; further in the case of textiles, bleeding of the tinting blue dye during washing results in an appreciable loss of whiteness.

An alternative approach to bleaching or blueing made its appearance in 1920, when Kraus applied a solution of aesculin, a naturally fluorescent substance found in an extract of chestnut, to increase the whiteness of textile materials. Although this method was used nearly 150 years before, this was the first time that a fluorescent material was applied specifically with the purpose of increasing whiteness. A drawback of aesculin is its poor light fastness; it decomposes rapidly under the action of light, leaving a yellow substrate.

2.1.2 Chemical structure and action of FWAs

After the discovery of the mechanism behind fluorescent whitening, a chemical compound was sought that could correct the drawbacks of natural aesculin. Many fluorescent compounds were patented in the years after Kraus's findings. Among these, were derivatives of coumarin, stilbene, benzoxazole, and benzimidazole. In 1935, ICI applied for a patent using stilbene as a whitening agent for cotton. In 1940, IG-Farben patented 4-4'-diaminostilbene-2,2'-disulphonic acid, a compound long used in dye manufacturing, as a whitening agent for cellulose fibres. In 1942 and 1945, respectively, CIBA and Geigy patented a series of benzoxazole and benzimidazole derivatives with improved light fastness. In 1964, CIBA and Geigy patented derivatives of amino-coumarin having strong affinity for both natural and synthetic fibres.

These compounds are today known as fluorescent whitening agents (FWAs). Their development in the post-war years has resulted in hundreds of different based products and in more than 700 brands available on the market.

FWAs can be regarded as chemical entities containing two different parts. The most important part is the fluorescent chromophore that can be any of a large list of compounds that absorb UV and short wavelength visible light and emit blue fluorescent light in the 400 nm to 500 nm region with a high quantum yield from 440 nm to 460 nm. This part of the molecule is not only important for its light production but it also must show chemical and photochemical stability (light fastness). Groups attached to the fluorescent chromophore constitute the second part of the FWA and have the purpose of improving its solubility properties and its affinity to different fibres and substrates. Since the action of FWAs is based on their fluorescence properties, the amount of light luminesced by the sample is strongly dependent on the amount of UV radiation in the irradiating source. Because most textile materials are viewed and used under natural sunlight the preferred source for evaluation is a good simulation of CIE D65 daylight illuminant.

2.1.3 Colorimetry of white

White is also a colour. In colorimetric terms it is a colour with very low saturation and very high lightness. Many methods applied in the past for assessing whites were based on single values of the reflectance spectrum, especially before the massive application of FWAs. It is now recognized that only methods that take the whole visible spectral region into account can really consider all different processes that produce a particular white perception [7].

While studying the positions occupied by different optically whitened materials on the chromaticity chart, it was noticed that all of them fall within a narrow region limited roughly by the dominant wavelengths 460 nm and 480 nm. Furthermore, whites can show also certain shades that are expressed by the colourist as being greenish or reddish, these corresponding to those samples situated closer to higher or lower dominant wavelengths. A neutral white, one that is neither reddish nor greenish, corresponds roughly to a dominant wavelength of 470 nm.

Many formulae have been devised to evaluate whiteness (W), with the goal of producing just one number that totally describes the perceived white. In general, these formulae take one of the following forms:

$$\begin{aligned} W &= f(X, Y, Z) \\ W &= f(x, y, Y) \\ W &= f(L, a, b) \\ W &= f(L^*, a^*, b^*) \\ W &= f(R, B, G) \end{aligned} \quad (1)$$

Note that all formulae are based on colorimetric quantities and thus take the whole visible spectral region into account. Expressing whiteness as just one number is however not a realistic way to approach the problem, since as with any other colour, different whites can also be differentiated in particular shade and lightness. For this reason a second number has been introduced that takes the shade into account and it is known as the tint value (T_w). The two numbers are interdependent and a material is deemed white only if the tint value lies within specified limits. Thus, the tint values must also be correspondingly expressed in the same colour system as whiteness.

$$\begin{aligned} T_w &= f(X, Y, Z) \\ T_w &= f(x, y, Y) \\ T_w &= f(L, a, b) \\ T_w &= f(L^*, a^*, b^*) \\ T_w &= f(R, B, G) \end{aligned} \quad (2)$$

Almost all published whiteness formulae can be classified according to this functional model. However, many of these earlier published formulae lack part of the information needed to assess white, and cannot express whiteness in a correct way, i.e. as it is perceived by the eye.

Continuing the observation made before, that all whites occupy a limited region of chromaticity space, a family of linear formulas has been developed that have the general formula:

$$W = D \cdot Y + P \cdot (x_0 - x) + Q \cdot (y_0 - y) \quad (3)$$

$$T_w = m \cdot (x_0 - x) + n \cdot (y_0 - y) \quad (4)$$

where x_0 , y_0 are the coordinates of the achromatic point. The formulae represent actually a family of indices, because parameters, D , P , Q , m and n must be specified. While D is related to the direct impact of lightness on whiteness, the other parameters are related to the dominant wavelength chosen, the influence of tint on whiteness and the corresponding scale factors. Two sets of parameters are normally in use, one determined by Ganz [8] and the other given by the Brookes [9]. Both parameters share the same dominant wavelength but have different scales and slightly different weighting of tint as it contributes to whiteness.

2.2 Fluorescent dyes in textiles and plastics

Fluorescent colorants are best known for their brilliance and their facility for obtaining higher chroma and lightness than non-fluorescent colorants. They have been used in safety notices, attention-getting advertising and to add to the colour gamut in mixtures with other colorants. They are also used in staining and tagging biological specimens. Since most of the early commercialized fluorescent colorants were not particularly lightfast, this stigma has been associated with fluorescent colorants in general. However, recent developments have made colorants available that are as lightfast as some non-fluorescent colorants even to the extent that select pigments have been successfully used in outdoor signs exposed to the weather for years.

The colour of fluorescent materials is dependent upon the quality of the illumination under which it is observed. The individual spectral excitation is a function of the colorant chemical structure. Although each colorant has its own excitation spectrum, many fluorescent colorants are excited by invisible ultraviolet radiation to produce emission spectra in the visible region. In addition, a number of violet and blue colorants are excited by visible light to give near infra-red energy which is not seen by human observers.

2.2.1 Fluorescent whitening (brightening) agents

This is the largest use of fluorescent colorants. Almost all laundry detergents and laundry bleaching materials contain a FWA. Many man-made fibres and most white papers contain a fluorescent whitening agent to enhance the appearance of the product by counteracting the yellowish cast of the natural or normal material with emitted blue light. There are a few chemical structures that are commercially available that in the main have a maximum excitation absorption at about 360 nm (near UV) and emit light in the region of 400 nm to 500 nm. For detergents, a water-soluble FWA is used which leaches out of the fabric when wetted. Water-soluble FWAs are also used with paper. Fibres and white plastics, on the other hand, are treated with water-insoluble FWAs. These fluorescent colorants are not particularly lightfast but their role in improving initial appearance does not demand higher performance.

2.2.2 Older fluorescent dyes

Rhodamines, Basic Violet 10 and Basic Red 1 and Eosin, Acid Red 87, and Fluorescein, Solvent Yellow 94, have been used in printing ink and for identification for nearly a century. They are fairly unstable and although highly chromatic cannot be used if there is any requirement for extended light fastness.

2.2.3 Encapsulated dyes

A substantial amount of the use of fluorescent coloration is achieved through resin-encapsulated types for safety products, attention-getting advertising, art forms and printed paper and film. Encapsulation renders what would otherwise be water-soluble dye into a form that is an insoluble particle or pigment. The basis for a line of pigments of this type is a yellow and a red dye which are used in an expanded colour range through various mixtures of the two colorants. A blue pigment in this category is made from a mixture of a blue pigment with a fluorescent whitening agent. A green fluorescent pigment colour is achieved with a mixture of the yellow fluorescent dye and an ordinary blue or green pigment. These pigments are of only moderate light fastness.

2.2.4 Basic dyes

When man-made acrylic fibres were developed they were found to be dyeable with basic dyes. Basic dyes are cationic dyes which are soluble in water and have a high affinity for the undried fibre. The poor fastness of traditional basic dyes was inadequate so dye chemists developed new basic dyes with special structures that had affinity for acrylic fibres. These dyes also have affinity for cationic-dyeable nylon. Among the special dyes that resulted from this research were a red and a yellow that are fluorescent as well as being much faster to light than the traditional colorants.

2.2.5 Disperse dyes

Disperse dyes are colorants with very limited water solubility and are used to dye polyester fibre through solid-state diffusion at elevated temperatures. A brilliant yellow dye of coumarin chemical family, Disperse Yellow 82, is highly fluorescent and has reasonable light fastness when dyed on polyester fibre.

2.2.6 Solvent dyes and pigments

This class of solvent dyes is not soluble in water and by certain criteria can be classified as pigments. There are a number of these colorants that are fluorescent: several yellows, oranges and reds. Among the fluorescent colorants are: Solvent Yellow 43, 44, 85, 98, 171 and 172; Solvent Orange 83 and 118; and Solvent Red 149, 150, 197 and 198. These represent a fairly wide range of selectable colour with the light fastness of individual colorants varying from excellent to moderate. For the most part these pigments are dispersed into various plastic media and the resulting mixture with the substrate affects the stability of the pigment.

2.2.7 Vat dyes

Vat dyes are normally applied to cellulosic fibres in a reduced state and are then oxidized to the water-insoluble pigment state after application. Since the colorant is actually a pigment, two colorants, Vat Red 41 and Vat Violet 1, have enough fluorescence to be called fluorescent pigments. These are fast to light.

2.3 Fluorescent materials in visual signalling

One of the major applications for fluorescent materials is visual signalling, in particular outdoor safety signing and markings. Fluorescent materials are able to make more efficient use of the available solar energy than are ordinary coloured materials due to their unique ability to absorb shorter wavelength solar radiation, and then to re-emit that energy as longer wavelength visible light. Their light emissive properties make fluorescent materials appear brighter and more colourful than ordinary materials under the same daylight illumination. As a result, fluorescent colours maintain a significant daytime visibility advantage over the corresponding ordinary colours in all types of weather conditions. Human factors research has demonstrated that luminance contrast and colour contrast both play roles in determining the relative visibility and conspicuity of objects in the environment [10-13]. The high visual contrast afforded by fluorescent signal colours makes them ideally suited for safety signing and marking applications. Indeed, the greatest luminance contrast, colour contrast, and hence greatest relative visibility and conspicuity of fluorescent materials occur under poor visibility conditions when the need is greatest.

Fluorescent signal colours encompass the hue range from red to orange to yellow to yellow-green to green. Numerous studies conducted over the years by maritime and transportation safety organizations have documented the exceptional outdoor visibility performance of fluorescent colours. These studies, which are well documented in the human factors and transportation safety literature, have established that under natural daylight illumination fluorescent coloured materials are detected with greater accuracy at longer distances and are significantly more conspicuous in the environment than their ordinary colour counterparts [14-22]. Based largely on the results of studies like these, many transportation and safety organizations specify that fluorescent materials must be used for a number of safety signing and marking applications. These applications include markings for slow and heavy vehicles [23, 24] navigational signs on waterways [25], industrial safety signing [26, 27], personal safety markings on roadway workers [28, 29], and some traffic control devices [30, 31].

Fluorescent materials have been around for more than 40 years, but it is only within the last few years that they have begun to achieve widespread acceptance in outdoor applications. Historically, the colour stability of fluorescent materials used for visual signalling has been very poor, often orders of magnitude lower than ordinary coloured materials. CIE 39.2-1983 on colours for visual signalling [31] warns that changes in the colour (hue) and luminance factor (brightness) of a fluorescent signal colour subjected to outdoor weathering "may be readily apparent in even a few days". Typically, the effective service life of

fluorescent materials used outdoors has been short, on the order of 2-3 years in a mild climate. However, these lifetimes were achieved only by allowing large chromaticity changes (fading in particular) and a significant decrease in the material's fluorescent light emission intensity. When subjected to continuous outdoor exposure under severe conditions (hot climate and high total solar irradiance) the actual service life has been considerably shorter, often on the order of months. In the last few years, fluorescent colorant systems with significantly improved photostability have been developed. Using modern technology it is now possible to produce materials with fluorescent colour stability approaching that of conventional colours. Fluorescent materials are now available that maintain their chromaticity and high level of fluorescent emission after years of exposure in severe climates. The end result is a redefinition of the contribution fluorescent materials can make towards improving the visibility and conspicuity of signing and markings. Given today's visually complex environments, one can expect increasing use of fluorescent materials for visual signalling, especially for critical safety applications such as traffic control signing, warning clothing for pedestrian visibility enhancement and industrial work place signing.

3. MEASUREMENTS OF TOTAL RADIANCE FACTOR

3.1 One-monochromator methods

As noted in the introduction, the total radiance factor of photoluminescent materials consists of two components, the reflected radiance factor and the luminescent radiance factor. The most direct way to measure the total radiance factor of a luminescent material is to illuminate the specimen directly with a full spectrum, i.e. polychromatic light with a relative spectral energy distribution near to that of the illuminant or source under which the colour specification of the specimen is to be evaluated [32]. The total radiance factor is then the ratio of the spectral radiance of the specimen at wavelength λ to the spectral radiance of the perfectly reflecting diffuser at the same wavelength. This process is similar to that for characterizing the reflectance factor of a non-photoluminescent material, except that there is no strict requirement on the spectral quality of the illumination coming from the light source. Traditional UV-VIS reflectance spectrophotometers [33] project monochromatic radiation onto the specimen. When the monochromator is between the light source and the specimen, the detector responds to reflected radiance at the wavelength of the monochromator and the luminescent radiance at all other wavelengths in the emission spectrum. When the monochromator is between the specimen and the detector, the detector responds to the reflected radiance and the luminescent radiance only within the bandpass of the monochromator.

As detailed in the section below, the amount of luminescent radiance will be dependent on the relative spectral distribution of the instrument source. The instrument source should thus be filtered or adjusted to have a relative spectral distribution that is similar to the relative spectral distribution of the source or illuminant under which the specimen or material will be used (see Section 5). If this is not possible, then the measured total radiance factor must be separated into its two components, the reflected radiance factor and the uncorrected luminescent radiance factor. This uncorrected luminescent radiance factor must be adjusted by the known mismatch between the instrument source and the desired illumination condition and then added to the reflected radiance factor to obtain the corrected total radiance factor.

There are four accepted ways to separate the total radiance factor into its components on a one-monochromator instrument [34]. They are the two-mode method [35], the filter reduction method [36], the adjustment method [37, 38], and the fluorescence-weakening method.

3.1.1 Fluorescence-weakening method

In the fluorescence-weakening method, the specimen is measured under three different spectral illuminating conditions. The spectral conditions are modified with a sharp cut-off filter between the illuminating source and the specimen. Two different filters are used. The first of these is a fluorescence-killing filter and is selected so that it has a transmission cut-off wavelength which is no more than 10 nm below the wavelength of maximum sample

emission; its transmittance is denoted $T_{\text{Filter-1}}$. The second filter is a fluorescence-weakening filter and is selected so that it has a transmission cut-off wavelength which is between 30 nm and 50 nm below the wavelength of maximum sample emission; its transmittance is denoted as $T_{\text{Filter-2}}$.

The spectral radiance factor of the sample is first measured over the range 380 nm to 780 nm with no filter in the beam, and these values are denoted β . The sample is then measured with the fluorescence-killing filter in the beam, giving β_1 and then with the fluorescence-weakening filter, giving β_2 . The reflected radiance factor of the sample, β_R is calculated as follows:

for wavelengths where:

$$T_{\text{Filter-2}} < 0,3$$

$$\beta_R = \beta$$

$$T_{\text{Filter-1}} \geq 0,3$$

$$\beta_R = (\beta_1 / T_{\text{Filter-1}})$$

$$T_{\text{Filter-2}} \geq 0,3 \text{ and } T_{\text{Filter-1}} < 0,3 \quad \beta_R = [(\beta_2 \times T_{\text{Filter-2}}) - (\beta \times k)] / [T_{\text{Filter-2}} - k] \quad (5)$$

and the constant k is calculated at the shortest wavelength for which $T_{\text{Filter-1}} > 0,3$ according to:

$$k = T_{\text{Filter-2}} [\beta_2 - (\beta_1 / T_{\text{Filter-1}})] / [\beta - \beta_1 / T_{\text{Filter-1}}]. \quad (6)$$

The constant k is wavelength independent and is the factor by which the total excitation energy of illumination on the specimen has been changed by the introduction of the fluorescence-weakening filter.

3.1.2 Two-mode method

In the two-mode method, the specimen is measured in a spectrophotometer that can operate in both monochromatic and polychromatic illumination mode, i.e. two modes of operation. The spectral curves that are recorded under the two illumination modes cross each other. The overlap region is where both absorption and emission occur simultaneously. The reflected radiance factor is then obtained by joining the short wavelength portion of the polychromatic mode radiance factor curve with the long wavelength portion of the monochromatic mode radiance factor curve by interpolation across the overlap region. The luminescent radiance factor is obtained by subtraction of the reflected radiance factor from the measured total radiance factor. Uncertainties in this estimation can be significant and spectrophotometers capable of two-mode operation are no longer manufactured.

3.1.3 Filter reduction method

In the filter reduction method, a series of linear long bandpass filters are placed, one at a time, in the light path between the source and the specimen. Each filter reduces the level of fluorescence, revealing a short portion of the reflected radiance factor. Three to five filters are usually enough to map out an estimate of the reflected radiance factor. The luminescent radiance factor is again obtained by subtraction. The uncertainty of the estimated reflected and luminescent radiance factors are much less than for the two-mode method.

3.1.4 Serial filter method

The serial filter method is similar to the filter reduction method but takes advantage of current technology and rapid computation methods. It is based upon successively altering the light source with a series of sharp cut-off filters so that the effect of the fluorescent emission on a polychromatically illuminated sample is sequentially reduced until it is finally eliminated. Typically 10-12 filters separated by about 25 nm are necessary to measure the entire visible spectrum. It has been shown that this method provides results comparable to the bi-spectral method (two-monochromator method) for several highly fluorescent plastic materials [39].

3.1.5 Adjustment method

In the adjustment method, a series of narrow bandpass filters spanning the visible spectral range are placed in the optical path between the source and the specimen. The source should have a spectral character similar to that of the illuminant under which the colorimetric evaluation of the specimen is to be performed. If the specimen is to be evaluated for CIE D65,