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Fluorescent Standards for Surface Colour

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This report describes work carried out for the National Measurement System Policy Unit under Project 9 - Spectrophotometry and Colorimetry: Fluorescent Standards for Surface Colour, NMSPU Reference MPU 8/23.2. The work was originally submitted in a proposal document dated February 1992.

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Approved on behalf of Chief Executive, NPL,
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CONTENTS

1	INTRODUCTION	 1
2	STABILITY OF FLUORESCENT MATERIALS	... 2
2.1	INVESTIGATION OF EXISTING MATERIALS	2
2.2	DEVELOPMENT OF NEW MATERIALS	2
3	SPECTROFLUORIMETER: CONSTRUCTION	3
3.1	SOURCE OPTICS	3
3.2	MONOCHROMATOR	3
3.3	SAMPLE OPTICS	4
3.4	DETECTION SYSTEM	5
3.5	POLARIZERS	... 5
4	SPECTROFLUORIMETER: TRACEABILITY	. 6
4.1	OPTICAL POWER MEASUREMENT	
4.1.1	Monitor detector	6
4.1.2	Reference detector	6
4.2	REFERENCE WHITE ..	
4.2.1	Sample/reference comparison	7
5	SPECTROFLUORIMETER: ACCURACY	8
5.1	ILLUMINATION NON-UNIFORMITY	8
5.1.1	Astigmatism compensation	8
5.2	ARRAY NON-UNIFORMITY .	 9
5.3	SAMPLE NON-UNIFORMITY	9
5.4	WAVELENGTH CALIBRATION	10
5.4.1	Input monochromator	.. 10
5.4.2	Array spectrometer	.. 11
5.5	NON-LINEARITY	11
5.6	STRAY LIGHT	
6	SPECTROFLUORIMETER: AUTOMATION	12
6.1	CONTROL HARDWARE	12

6.2	COMPUTATION OF RESULTS	12
7	SPECTROFLUORIMETER: RESULTS	15
8	SPECTROFLUORIMETER: CUSTOMER SERVICE	16
APPENDIX	Spectrofluorimeter theory	17
ADDENDUM	Recent developments	18

INTRODUCTION

This report describes work undertaken for the National Measurement System Policy Unit in a project to provide fluorescent standards for surface colour. The proposal contained three principal elements:

- i) The development of stable fluorescent materials
- ii) The development and construction of a reference instrument
- iii) The evaluation and characterisation of the developed materials.

The construction, evaluation and commissioning of the instrument have been carried out by the NPL during the period Sept 1993 - March 1995, with funding from the NMSPU. The instrument has been developed to a stage where a calibration service is available for both customer materials and transfer standards. Compared with equipment previously available, the new instrument obtains more comprehensive measurements with less operator intervention at considerably higher speed. It therefore represents a significant advance in cost-effectiveness.

Existing fluorescent samples in a varied collection have been shown to be stable over a period of one year if they are stored in the dark and only exposed to light during measurement. For the development of new materials with improved stability in daylight, an extra mural research agreement was to be placed by the NPL with the Loughborough University of Technology, who have appropriate expertise in both the field of fluorescent materials and in the production of standard samples. This work would be funded by a club consisting of interested parties from industry.

Efforts to obtain sufficient support have resulted in less than a quarter of the necessary funding being found. As an interim measure, sets of existing fluorescent standards which can be calibrated on the reference instrument and issued to industry have therefore been obtained from a supplier in the USA. Although these are not stable under continuous ultraviolet irradiation, NPL is now in a position to supply them to industrial customers for commercial instrument calibration. They must be kept in the dark and used only a few times a year.

2 STABILITY OF FLUORESCENT MATERIALS

2.1 INVESTIGATION OF EXISTING MATERIALS

A total of 20 white samples with varying degrees of optical brightening and 9 samples from various sources having a variety of fluorescent colours have been measured, kept in the dark for a period of a year and measured again. The measurements were made on an instrument in which the dispersion occurs after the sample and there is no integrating sphere, both of which are essential requirements for this type of measurement. The spectral distribution of the illumination was an approximation to that of daylight and therefore adequate for the investigation of small changes. The largest change ΔE , which is a measure of colour difference, was 0.17 for the white samples and 0.67 for the coloured samples, in the case of a very bright yellow.

Similar sets of white and coloured samples were measured before and after exposure to 100 flashes of pulsed xenon light, as often used in conventional colour-measuring spectrophotometers. Again the changes ΔE were small. Since a change which can just be detected visually corresponds to a change ΔE of between 0.5 and unity, these results demonstrate clearly that in general fluorescent materials are stable over a period of one year if they are exposed to light only when measurements are made on them.

Further sets of samples were continuously exposed for several hours to a high power xenon lamp, whose light includes a considerable amount of the ultraviolet radiation which is responsible for the degradation of fluorescent materials in daylight. Changes ΔE in excess of 0.5 after 100 hours irradiation were noted.

2.2 DEVELOPMENT OF NEW MATERIALS

For the development of stable fluorescent materials, efforts have been made to form a Club consisting of interested parties who would jointly fund the project.. Possible companies to approach were identified from the NPL customer base and Spectrophotometry and Colorimetry Club membership, and from trade directories; £10k was suggested as the contribution from each participant, spread over two years. Only two companies have been found who are prepared to contribute this amount, representing less than a quarter of the £90k needed. As an interim solution for the provision of transfer standards, twelve sets of 8 standard plastic tiles with differing degrees of whiteness and twelve sets of 3 coloured tiles - red, orange and yellow - have been purchased from a US source (Frederick T Simon Inc). However, the cosmetic quality is poor and the colours are unlike those encountered in practical use. The tiles are not stable when subjected to continuous ultraviolet radiation.

3 SPECTROFLUORIMETER: CONSTRUCTION

The spectrofluorimeter has been constructed as described in the proposal, and is shown in the accompanying photograph. It consists of a xenon arc source, a double monochromator, a motorized slide to select sample or reference white and a diode array spectroradiometer to record the complete reflected/emitted spectrum for each incident wavelength. Polarizing filters to simulate unpolarized light have been incorporated, and also cylindrical lenses to cancel the astigmatism due to the rest of the optics. A departure from the proposal, taking advantage of recent developments, is the use of a calibrated solid state detector rather than a calibrated source to obtain absolute values of optical power. The diode array system enables a set of measurements on sample and reference white to be recorded and fully processed within 15 minutes.

3.1 SOURCE OPTICS

The instrument has been assembled on a 2 m x 1 m optical table, providing good stability of the optical paths and convenient fixing arrangements. Figure 1 shows the layout of the principal components, approximately to scale. The source is a 75 W "ozone free" xenon arc lamp (Osram), which has a relatively high radiance over the spectral region of interest, particularly in the near ultraviolet. It is contained within a fan-cooled housing with a fused silica window, and has a separate stabilized current power supply which incorporates the high-voltage striker unit (Knight Optical Technology). Since the inner wall of the lamp gradually becomes blackened, it needs to be replaced after about 400 hours of use; an additional control box incorporating an elapsed time counter has therefore been constructed, the timer being switched on manually when the lamp is struck. The box also has a master power switch which allows the cooling fan to continue running when the lamp has been switched off. The lamp will be replaced by a "super quiet" equivalent (Hamamatsu), which gives superior stability and lower noise, while having a longer life of 1000 hours.

The arc is imaged onto the entrance slit of the monochromator by Mirror 1, which is the first of three similar concave spherical mirrors (Optiglass). To minimize optical aberrations, the radius of curvature of 560 mm is the largest which can be accommodated on the optical table, while the diameter of 150 mm allows the aperture of the monochromator to be overfilled comfortably. The mirrors are coated with aluminium and an overcoating of silicon dioxide, which provides protection while transmitting the ultraviolet. The mirror mount (Daedal) has fine-pitch tilt screws for horizontal and vertical positioning of the image, and is carried on a micrometer-driven slide (Ealing) with a range of 25 mm for focussing. In principle it would be better to move the source for focussing, since the effects of pitch and yaw on the image position would be very much less, but movement of the mirror is more convenient in use and the precision construction of the slide makes the image wander negligible. To minimize aberration, the source is displaced by the minimum possible amount from the slit, both laterally and longitudinally. The lateral displacement of 90 mm produces a vertical astigmatic line image about 2 mm long at the slit.

3.2 MONOCHROMATOR

The monochromator (Spex), which enables the sample to be illuminated by one wavelength at a time, is a double design of medium size with two stages in series. Any stray light from the exit of the first stage at wavelengths other than that required is dispersed by the second stage, reducing the amount at the final output to a very low level. The instrument is designed as a single unit, rather than as two single monochromators in series. This avoids the need for transfer mirrors between the two stages, and yields a convenient optical geometry with the monochromator at the centre of the table separating the input and output halves of the system.

One of the monochromator gratings is turned by a precision leadscrew and stepper motor, linked to a revolution counter, the second grating being coupled to the first mechanically by a phosphor-

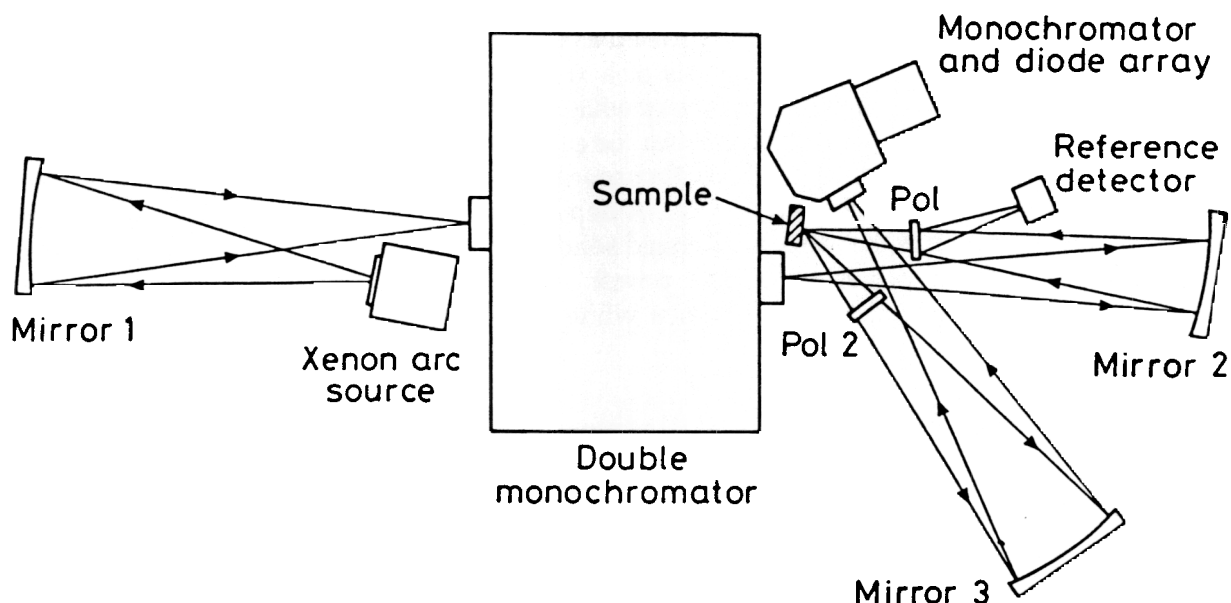


Figure 1 Layout of spectrofluorimeter

bronze belt. As gratings with a standard pitch of 1200 lines/mm are fitted, the counter gives a direct reading of the wavelength in nanometres. An order sorting filter which can be removed by energizing a small rotary solenoid has been added to the standard instrument inside the exit slit. The dispersion at the exit slit is 1.8 nm/mm.

Another rotary solenoid (RS Components) carries a blade of black card which blocks the beam entering the monochromator when the solenoid is energised. Although it is designed to operate from 12 V, counterbalancing has allowed reliable operation from a small 5 V supply.

3.3 SAMPLE OPTICS

The exit slit, on the opposite side of the monochromator to the entrance slit, is imaged onto the sample by Mirror 2, placed at the other end of the table. Again the separation of the image from the slit is as small as is practicable, about 90 mm. The patch of light on the mirror surface, as restricted by the monochromator optics, is about 100 mm square, giving an f /number of 4.0 when measured along a diagonal. To facilitate the positioning of the surface of the sample to be normal to the incident beam, the square matrix of tapped holes in the surface of the optical table is used as a reference; the centre of the mirror and the image on the sample are arranged to lie on one of the lines of holes parallel to the long axis of the table.

Light reflected or reemitted by fluorescence from the sample at 45° is received by Mirror 3, which forms an image of the illuminated patch on the sample surface at the entrance to the diode array spectrometer; the lateral separation in this case is 70 mm. The centre of this mirror and the patch on the sample are arranged to lie on a diagonal line of holes. The items are mounted on rigid supports, arranged so that the centres of all optical beams are at a height of 220 mm above the surface of the table.

3.4 DETECTION SYSTEM

The diode array spectrometer (Oriel) is smaller than the input monochromator. It has a single holographic grating with 400 lines/mm, giving a dispersion of 0.18 nm/mm, one tenth of that of the main monochromator, at the array surface. The diode array system (Andor Technology) uses a linear array (Hamamatsu) which has 1024 elements in a length of 25 mm, so that each element is 0.25 mm wide and spans a spectral range of 0.5 nm. The total spectral range of interest, 320 nm to 780 nm, nearly fills the length of the array. The surface of the array is tilted to minimize the reentering of reflected light and the half used for longer wavelengths is covered permanently by an order sorting filter. The array can be temperature controlled to stabilize the dark current. Peltier cooling is provided to reduce the temperature and therefore the noise, but there is a risk that the array will be damaged by condensation and it has been found that adequate results can be obtained without cooling. The array data processing and all system control functions are performed by a personal computer (Dell), which contains the array electronics on a plug-in card.

The width of a spectral line image on the array can be defined in two ways. If the array spectrometer is used without an entrance slit, the width is determined by the illumination line on the sample, which is in turn determined by the setting of the monochromator exit slit. If the spectrometer has an entrance slit, this determines the width and the monochromator exit slit is set to overfill it generously. The relative merits of the two alternative arrangements are discussed later in the section on 'Accuracy'. Because the linear dispersion of the monochromator is about ten times that of the spectrometer, the bandwidth of the light in the spectral line image is only one tenth of the wavelength range that it spans on the array.

3.5 POLARIZERS

Measurements need to be made for a defined state of polarization of the light incident on and coming from the sample. However, the spectral energy distributions of the horizontally and vertically polarized components from the monochromator have been found to be very different. There is a particularly strong grating anomaly at about 400 nm, causing the energy in one of the components to fall almost to zero. Polarizing filters are therefore placed in the incident and emergent beams, with no other optical components between the filters and the sample. Both filters have their polarization axes set at 45°, which makes the horizontal and vertical components equal in intensity and therefore equivalent to unpolarized light.

The polarizers (Meadowlark Optics) consist of sheet polarizing material cemented between pairs of parallel-sided optical flats, 50 mm in diameter. These are relatively expensive items intended for use in interferometry, but were found to show much better extinction when crossed than a cheaper equivalent. On the input side, Pol 1 has a special polarizing sheet for ultraviolet use and uncoated fused silica flats; for the output side, Pol 2 consists of standard visible polarizing material and antireflection-coated glass flats. The transmittance of the visible material (Pol 1) was measured to be about 38% in the visible region and the ultraviolet material (Pol 2) slightly lower, which is as expected. In the ultraviolet region, the ultraviolet material falls to about 16% at 350 nm and the visible material to about 8%. While the diode array is not required to detect below 380 nm for measurement purposes, the finite amount of light transmitted by Pol 2 is useful for diagnosing the system behaviour.

To set each of the polarizers accurately to 45°, an auxiliary polarizer in a rotatable mount graduated in degrees is introduced. A white light source is viewed through the two polarizers in series, and the auxiliary polarizer is rotated to the crossed position where no light is transmitted. It is then reversed back-to-front by turning it on its vertical mounting pin, and again rotated to the crossed position. The angle of rotation needed should be 90°. If it is not, the polarizer to be set is turned through one half of the error angle and the test is repeated.

4 SPECTROFLUORIMETER: TRACEABILITY

4.1 OPTICAL POWER MEASUREMENT

The power in the light beam falling on the sample is measured by a silicon diode trap detector. When used in conjunction with the reference white, this also enables the sensitivity of the array to be determined. If the detector were used directly during a measurement run, it would have to be exchanged physically with the sample or reference white for each incident wavelength, which would increase the total time considerably. Therefore a small proportion of the beam is directed to a second trap detector which is used during a run, the ratio of the outputs of the two detectors being determined in a separate calibration.

The trap detectors are produced in-house by NPL Radiometry Section. Each detector contains three 10 mm square silicon photodiodes (Hamamatsu), arranged so that light reflected from the surface of the first is directed to the second, and from the second to the surface of the third at normal incidence. Any remaining reflected light is then returned to the second and first. The device has a quantum efficiency of about 0.995 for visible radiation, falling to a minimum of 0.95 at 360 nm and then rising again. The responsivity of the detector used at the sample position has been calibrated by Radiometry Section over the working wavelength range of 320 to 780 nm; the uncertainty of the calibration is 0.1% from 780 nm to 410 nm, 0.5% from 400 nm to 390 nm, and 1% from 380 nm to 320 nm. The photocurrents are measured by a precision d.c. amplifier (Vinculum) incorporating a 4½ digit voltmeter with a parallel interface (Newport) which is connected to an input/output card (National Instruments) fitted in the computer.

Monitor detector

To keep the number of optical components to a minimum, the polarizer Pol 1 also serves as a beamsplitter to reflect a small proportion of the light to the monitoring trap detector, shown as Reference detector in Figure 1. Conveniently, the uncoated silica surfaces of Pol 1 reflect about 4%. The reflected beam is directed at an angle of about 25° to the main beam, sufficiently oblique to ensure that the main beam is not obstructed. Beams are reflected from both outer surfaces, and the one which has passed twice through the filter is selected. This beam is the weaker of the two, but is polarized in the same manner as the beam incident on the sample. This is desirable because the state of polarization of the light from the monochromator does not then affect the ratio of the intensities of the selected beam and the main beam. This ratio depends mainly on the spectral transmittance of the polarizing material.

If the trap detector is simply placed at the focus of the reflected beam, the cone angle of the beam is too large to ensure complete collection of the light. Therefore a planoconvex fused silica lens with a focal length of 25.4 mm (Ealing) reimages the focus with a magnification of about three, reducing the cone angle by the same factor. If the array spectrometer is used with a slit at its entrance, a similar slit is placed at the prime focus so that the light seen by the trap detector corresponds to that seen by the array. The slit surround also serves to block the reflection from the second outer surface of the polarizer, and the weaker one from the surfaces of the polarizing material itself, which is separated laterally by an adequate amount as the polarizer is 13 mm thick. If the spectrometer has no slit, a vertical edge is used so that all the light in the wanted beam passes to the detector. A small white patch bordering the edge allows the unwanted beams to be seen, so that one can readily check that they are completely blocked while the wanted beam is completely transmitted.

Reference detector

When the second trap detector is used to measure directly the power in the influx beam, there is no other beam to be blocked but space is restricted in the longitudinal direction. In this case

a planoconcave fused silica lens, focal length 25 mm (Newport), is used to reduce the cone angle, at the same time shifting the prime focus somewhat further along the axis. Any variation in the transmittance of this lens with wavelength must be allowed for. The normal incidence reflection losses at the lens surfaces give theoretical transmittances of 92.5 % at 320 nm and 93.2 % at 780 nm; the effects of obliquity at the edges of the beam are negligible, as is absorption in the body of the lens. The spectral transmittance has been checked experimentally by reducing the cone angle sufficiently for the light to be fully trapped without the lens present and taking the ratio of the detector signals with and without the lens. The theoretical values were confirmed to within the accuracy of measurement, and they are therefore used to allow for the insertion loss.

Each trap detector is mounted on a linear micrometer-driven horizontal slide carrying a column of adjustable height (Ealing), so that the transverse position can be adjusted. Below the detector is an optical mount (Spindler and Hoyer) providing adjustment of pitch and yaw. The longitudinal movement of the detector accompanying pitch adjustment does not affect the overall adjustment significantly. It is found that over a transverse range of about 3 mm the variation in signal is less than 0.3%, but there is a relatively rapid fall-off for larger movements; this demonstrates that the whole of the light beam is being trapped adequately. Stray light entering the detector can produce large spurious signals, so the path between the transfer lens and the monitoring detector entrance is shielded by opaque plastic covers.

4.2 REFERENCE WHITE

The white surface of known reflectance with which the sample is compared is a mounted piece of Spectralon (Labsphere), a proprietary thermoplastic resin material whose characteristics are close to those of a perfect diffuser over a broad spectral range. The spectral reflectance has been measured relative to the reference scale currently used by the NPL. There was no significant evidence of variation with wavelength and a constant reflectance of 0.995 has been adopted. This has an uncertainty of 0.007, mainly due to the uncertainty in the reference scale which is obtained from the PTB in Germany.

4.2.1 Sample/reference comparison

To provide rapid interchange of sample and reference under computer control, a custom mount has been constructed by NPL workshop and fitted to a linear stage moved by a lead screw and stepper motor (Time & Precision). The movement is vertical, as this allows the separations between monochromator exit, specimen and spectrometer entrance to be relatively small. The sample is located above the reference white, so that it can be inserted easily and large sizes can be accommodated. The front working surfaces of sample and reference are spring-loaded against a vertical plate which has suitably-sized apertures, the sample being held by a slightly modified arm from a commercial instrument (Datacolor). The face of the plate is lined with a thin sheet of soft white plastic, to minimize contamination of the surfaces of the samples.

Because the sample and reference surfaces are illuminated normally but viewed obliquely, out-of-plane movement produces a sideways shift of the image on the diode array. Provision has therefore been made to adjust the mounting plate so that the two surfaces lie in the same plane when in the working position. The plate is held along its bottom edge by a strip hinge and tilted by an adjustment screw located between sample and reference. Since this moves the sample much faster than the reference, it is straightforward to make an iterative adjustment. Using this screw in combination with the horizontal adjustment screw on Mirror 3, and with the monochromator slit narrow and the spectrometer slit removed, the system can be set by viewing the array output so that the image is positioned correctly in the spectrometer entrance for both sample and reference.

5 SPECTROFLUORIMETER: ACCURACY

In a reference system of this kind, it is particularly important to minimize possible errors due to non-uniform spatial distribution of the light, or of detector sensitivity. With double dispersion, the amount of light reaching each detector element in the array is rather low, so that introduction of optical diffusion would prevent operation to sufficient accuracy at the speed which is required. Careful consideration of the effects of non-uniformity is therefore needed.

5. ILLUMINATION NON-UNIFORMITY

In the horizontal direction, the considerations depend on whether a slit is used at the array spectrometer entrance. Without a slit, the whole of the light across the line on the sample is received by both the array and the trap detector, which should minimize error. However, if there is lateral diffusion of the light in the sample surface or it has structure, the width of the line image on the array is broadened so that it spans a band of more than 5 nm. Also, an inward or outward movement of the sample surface or a horizontal rotation of Mirror 3 produces a movement of the image along the array and an error in the wavelength calibration, so that it must be repeatedly checked. When a slit is present, it defines a fixed position for the line on the array and these problems are eliminated.

The dispersed energy at the monochromator exit is very uniform horizontally, provided that the output of the source is not changing rapidly with wavelength. This has been demonstrated by opening the output slit of the monochromator wide, placing a vertical strip of paper about 1 mm wide at the sample position, scanning the slit image across it by means of the horizontal control on Mirror 3, and observing the constancy of the output of the diode array with its spectrometer slit removed. It follows that the energy received during a measurement with the slit present is not influenced by small rotations of Mirror 3 or surface height variations of the sample.

The above considerations favour operation with the spectrometer slit present. However, it is difficult to be sure that the ratio of the energy passing through the spectrometer slit to that passing through the monitor detector slit is the same at all wavelengths, or to determine the correction if it is not. Initial trials were therefore performed with the slits absent.

In the vertical direction, the sensitive region of the diode array has a height of 2.5 mm. This should either be overfilled or underfilled, so that the amount of light received is not dependent on the precise vertical adjustment. With the basic optical system, the array is overfilled by an astigmatic line which is formed by convolution of the line on the sample with the astigmatism of the optics following it. For the line on the sample, the vertical distribution corresponds to horizontal compression of the distribution over the monochromator aperture. This is likely to have a non-uniformity which is dependent on wavelength, due to optical aberrations and grating imperfections, and such a wavelength dependence has been demonstrated by experiment. Underfilling of the diode array is therefore preferable, provided that the sensitivity in the vertical direction is spatially uniform.

5.1.1 Astigmatism compensation

To obtain the underfilled condition, the astigmatism occurring before and after the sample is cancelled by means of two plano-convex cylindrical lenses made from fused silica (Spindler and Hoyer), the focal length of 310 mm being about the largest that is readily available as a standard item. The first of these is placed in the beam from the monochromator exit slit and adjusted longitudinally until the image on the sample, as viewed by a hand lens, has minimum height. A significant amount of vertical flare can still be seen, so this has been blocked by placing a 1.25 mm horizontal slit to coincide with the horizontal astigmatic line which lies outside the monochromator exit slit. The beam diverging from the monochromator is higher than it is wide,

so in this position the lens makes it squarer. The second cylindrical lens is placed in the beam directed to the spectrometer entrance. Both lenses can be rotated in their own planes, being adjusted so that the image width seen by the diode array, with the spectrometer entrance slit removed, is minimized.

Longitudinal focussing of the second lens is less straightforward. Since it is to compensate the astigmatism introduced by the array spectrometer, the array signal itself must be used to perform the adjustment. If the light reaching the array lies entirely within its sensitive area, changes in the length of the vertical length of the astigmatic line will not affect the signal. For the procedure devised, the image is positioned on the bottom edge of the array so that the signal has about half its maximum value. An aperture about 50 mm in diameter is then moved vertically over the central region of the face of Mirror 3. This changes the direction of the beam converging to the image patch, causing it to move if the focus is incorrect. The array signal amplitude then shows corresponding changes, with a reversal of sign for the other side of the focus, correct focus being achieved when the signal remains constant.

5.2 ARRAY NON-UNIFORMITY

With the focus correct, uniformity of sensitivity of the array in the vertical direction can be readily checked by moving the image over the sensitive area, using the vertical tilt control of Mirror 3. With the mirror aperture reduced by a 90 mm mask so that the spectrometer optics are underfilled, the signal remains constant to within 0.3 %. With the mirror unmasked and the optics overfilled, a linear variation of about 5 % is observed, indicating that vignetting is occurring in the spectrometer. Since this is independent of wavelength and is common to sample and white, it should not affect the accuracy of the measurements.

In the horizontal direction, for which the spatial resolution is set by the diode spacing of 25 μm , good uniformity is observed if the spectrometer slit is removed and a white diffuser is placed near the entrance to flood the system with light. However, using the monochromator with its exit slit set wide so that a band of pixels is illuminated, some irregularities can be seen. If the aperture of Mirror 3 is reduced by a mask, the amplitudes of these irregularities increase, and when the aperture is moved horizontally they move slightly along the array. These observations indicate that the irregularities are caused by dust particles on the window of the array, the movement being due to parallax. The optimum strategy to minimize possible errors due to dust or vignetting is therefore to mask Mirror 3 so that the spectrometer aperture is just underfilled.

Comparison with the reference white should substantially eliminate systematic errors, as the same optical path is used for sample and reference. Since a large patch of light can be regarded as a synthesis of similar small ones, it follows that correct results will be obtained with a light patch having a finite extent in the vertical direction, provided that all of the returned light is collected with equal efficiency. This remains true if the lateral spread is different in the sample and the reference white, and it will be true for a fluorescent sample as well as a passive one if saturation is insignificant. This assumption can be checked by repeating a measurement with the image defocussed until it nearly fills the array vertically. Use of a small light patch means that spatial non-uniformities of sample or reference white are not averaged, but a degree of averaging can be achieved by moving the sample slide during the time that the diode array is being exposed.

5.3 SAMPLE NON-UNIFORMITY

A requirement to measure specimens with structured non-uniform surfaces necessitated a modification to the optical arrangement which would enable a larger area of the surface to be sampled. The surface relief on the specimens consisted predominantly of lines in two directions at right angles with a spacing of about four lines per millimetre, and structure with a coarser scale was also apparent although less pronounced. Mirror 2 was therefore moved axially by 10 mm,

so that the slit image moved away from the sample surface by 20 mm and the illuminated patch increased in size to about 4 mm square. The trap detector and its associated optics were also moved 20 mm so that the whole of the incident power was still monitored.

Mirror 3, imaging the sample onto the spectrometer, was defocused by a comparable amount, making the array surface conjugate to a plane in space some distance in front of the specimen surface. The variation of radiance over this plane is much smoother than over a surface close to the specimen, so introduction of a limiting aperture should ensure that the flux reaching the array pixels is proportional to the average reflectance of the illuminated patch. In the horizontal direction, use of a slit at the spectrometer entrance is now essential to define the bandwidth. For the vertical direction, a 0.5 mm horizontal slit was also introduced at the spectrometer entrance, similar to that at the monochromator exit, causing the 2.5 mm height of the array to be underfilled. These slits in combination define a small virtual rectangular aperture in front of the sample through which light is collected from it. The directions of the rays from different parts of the illuminated patch are different, but the range of directions is about the same as in the focused condition.

In this arrangement, aperture and field have been interchanged, and the light filling the spectrometer aperture is now a somewhat blurred image of the patch on the specimen. As the amount of defocus increases, the array signal remains (almost) constant until this image decreases to a size such that it underfills the spectrometer aperture, when the signal decreases. With this condition, light is collected equally efficiently from the whole area of the illuminated patch, apart from the effects of non-uniformities in the spectrometer optics. The horizontal slit reduces the amount of blurring of the top and bottom edges, enabling the condition to be properly achieved.

The arrangement inevitably gives considerably lower array signals, the reduction being roughly proportional to the increase in area of the illuminated patch, but it has considerable advantages in addition to averaging over a more realistic surface area. Any change in the size of the patch due to change of focus with wavelength will remain the same, but because the patch is larger the fractional change will be considerably reduced. The use of a slit still has the advantage that the image on the diode array is independent of small distortions or movements of the patch on the sample, but in this case there is not the associated uncertainty in the applicability of the trap detector calibration. If the signal levels are adequate, it appears preferable to use this mode of operation even for uniform samples.

5.4 WAVELENGTH CALIBRATION

Input monochromator

The wavelength drive mechanism of the monochromator is linked to a mechanical revolution counter which provides a direct reading of the wavelength value. To calibrate this, a low pressure capillary discharge mercury lamp is substituted for the xenon lamp. This provides narrow spectral lines with known wavelength values at

302.15, 365.02, 404.66, 435.83, 546.08, 576.96, 579.07 nm.

Second order diffraction of the first three of these effectively provides further lines at

604.30, 730.04, 809.32 nm.

To perform the calibration, a silicon photodiode with enhanced ultraviolet sensitivity (Centronics) is placed close to the output slit so that it collects all of the emerging radiation. The input and output slit widths are both set to 0.4 mm, corresponding to a bandwidth of 0.7 nm. The photodiode is connected to the amplifier normally used for the trap detector. For each spectral

line, the monochromator is slowly scanned using the manual control buttons and readings are taken of the peak and background currents. The monochromator is then set on one flank of the line so that an intermediate current is obtained and the wavelength value is recorded, followed by the value corresponding to the same current for the other flank. The mean of these two wavelength values is compared with the expected value for the spectral line.

This process gives a wavelength uncertainty within 0.15 nm. A calibration run gave a monochromator wavelength error ranging from -0.02 to -0.32 nm, and backlash was found to be less than 0.1 nm. It is therefore adequate to apply a constant offset, in this case +0.17 nm, during measurements.

5.4.2 Array spectrometer

Since the wavelength calibration of the double monochromator is accurate and repeatable, it is used in the calibration of the array. A series of eleven wavelength settings from 350 nm to 750 nm at 40 nm intervals is fully adequate, as the array calibration is nearly linear. For each wavelength setting, an array scan is recorded. The number of the pixel with the highest signal count is found, this being close to the centre of the peak corresponding to the reflected light. The position of the centre of gravity of the peak is then calculated in units of pixel number. Assuming that the wavelength at this position corresponds to the monochromator setting, the wavelength value for the pixel with the highest count can then be found. The set of pixel numbers with their associated wavelength values are printed. The values are then used in conjunction with the calibration software facility provided with the array to set up the wavelength scale. Subsequently, continuing agreement between the monochromator and array calibrations provides a good indication that neither of them has drifted.

5.5 NON-LINEARITY

To check the linearity of the current signals from diode array or trap detector, a rigid vertical bar 12 mm wide is mounted centrally over the aperture of Mirror 2, dividing it into two halves. Current readings are taken, and are repeated with a card mask placed over one half and then the other half of the aperture. A background reading is subtracted from each of these three readings. The sum of the currents for the two separate apertures should equal that obtained when they are combined. Provided that the edge of the card lies within the area of the strip, its precise position does not affect the aperture boundaries. For both array and trap, linearity within 0.2 % was found for the highest signal levels used during a measurement.

5.6 STRAY LIGHT

The level of stray light on the diode array due to unwanted reflections and scattering in its associated spectrometer was checked by the usual method for this type of instrumentation. The xenon source was temporarily imaged directly onto a slit placed at the position normally occupied by the monochromator exit slit. A polychromatic image could then be formed on the reference white, producing a xenon spectrum on the array. An orange cut-off filter (Hoya 52Y), which only transmits wavelengths longer than 520 nm, was placed in the beam illuminating the reference white. 1000 array scans were summed in order to obtain a noise-free picture of the residual array signal at wavelengths below the cut-off. The signal was about 1/1500 of that above the cut-off. For a yellow filter (Hoya 44Y) with cut-off wavelength 440 nm, the corresponding figure was 1/700.

When the input monochromator is set to a particular wavelength, its double construction should make the light at other wavelengths negligible. The apparent signal spread on the diode array surrounding a single wavelength peak was examined, again by summing 1000 scans. The signal was 1% of the peak value at a position 7 nm from the peak, and 0.1% at 20 nm.

6 SPECTROFLUORIMETER: AUTOMATION

6.1 CONTROL HARDWARE

The monochromator is fitted with an electronic board which enables its wavelength-scanning motor to be stepped directly by TTL logic pulses. This avoids the complication and possible difficulty associated with driving via an interface, and ensures that the number of steps executed by the motor is known precisely. The drive pulses are supplied by one of two outputs from a "breakout box" providing connection to the diode array electronic board via opto-isolators. Sending an "on" or "off" instruction causes the output to go high or low, the motor being stepped by a high-to-low transition. A movement of 5 nm requires 250 steps, so that the maximum recommended speed of 500 steps per second corresponds to a minimum scan time of 0.5 s. In practice 1.5 s is used, to ensure that no steps are missed.

Binary switching operations are performed by a reed relay card (Amplicon) fitted into the computer. This carries two groups of eight relays with two different addresses, six relays in one of the groups being used. When a number is sent to the associated address, the 0's and 1's in the binary equivalent of the number determine which relays are open and closed. For example, the number 12 with binary equivalent 1100 causes the third and fourth relays to be closed and all others to be open. The functions of the six relays are -

1. Background shutter (open / closed)
2. Order sorting filter (out / in)
3. Monochromator drive direction (wavelength increasing / decreasing)
4. Sample slide drive direction (upwards / downwards)
5. Sample slide drive motor (on / off)
6. Sample slide drive motor (energised / deenergised).

The states in parentheses correspond to the relays being: open (0) / closed (1). This approach achieves a compact control system at comparatively low cost and again avoids the complexities associated with interfacing. The reed relays provide electrical isolation of the computer from the rest of the system, greatly reducing the risk of damage.

A manual control box has also been constructed, so that the system can be operated without the computer or it can be overridden. The box incorporates an oscillator based on a 555 timer integrated circuit for driving the monochromator; this is powered by the 5V supply which energises the background shutter. Pushbuttons are used rather than switches, to ensure that they are left in the particular state which allows correct operation by the computer. There are six pushbuttons, which when depressed perform the following functions -

1. Raise sample slide
2. Lower sample slide
3. Increase monochromator wavelength setting
4. Decrease monochromator wavelength setting
5. Insert order-sorting filter
6. Insert background shutter.

In addition, two double-throw switches enable the sample slide position and monochromator wavelength to be altered at much reduced speed, so that precise settings can be made.

6.2 COMPUTATION OF RESULTS

The computer programs use the software facility provided with the diode array system. This allows the whole of a stored image from the array to be treated as a single variable, and selection of a particular element from a store is easy. The main program used for a measurement calls a number of subroutines, which facilitates comprehension and modification. The principal subroutines are:

Bgrun This stores a record from the diode array with the background shutter closed. The dark current and any spurious signal due to background light can then be subtracted from subsequent readings. A reading is also taken from the trap detector voltmeter for similar use.

Bgavg After initial use of **Bgrun**, it was discovered that the dark current values obtained from an array scan depend slightly on the time that has elapsed since the previous scan. Also, the random noise component in a single background scan becomes greatly amplified when the 93 measurement scans from which it is subtracted are added together. **Bgavg** therefore takes the average of several initial background scans, separated by a time interval equal to that between successive measurement scans.

Sigrun This takes values from the array and from the trap detector voltmeter for each wavelength setting of the monochromator and subtracts the values obtained by **Bgavg**.

Mono This sends a stream of 250 pulses to the monochromator stepper motor after each successive array capture, causing the wavelength setting to change by 5 nm.

Bands This sums the corrected array element values over 5 nm intervals, which are centred on the wavelength values to which the monochromator is set. Thus the spectral peak due to reflected light is always centred symmetrically in an interval. Since each pixel spans about 0.5 nm, there are approximately ten pixels in each interval. For a pixel lying on the boundary between two intervals, its signal is divided between them in appropriate proportions. This procedure eliminates any requirement for interpolation, as the data are subsequently multiplied by values from standard tables which are also given at 5 nm intervals. The quantity of data is reduced by a factor of ten and the signal-to-noise ratio is improved.

Shift After application of **Bgavg** and **Bands**, the sets of array scans show significant irregular drifts of zero level which are virtually the same for all intervals from a particular scan. The subroutine **Shift** substantially eliminates these drifts, exploiting the fact that all results have some spectral regions where there is no signal due to either reflection or fluorescence. The routine first finds the lowest value. It then takes the mean of all values which exceed the lowest one by an amount slightly greater than the peak-to-peak noise. This mean is subtracted from all values to remove the offset.

Shinit This sets up the threshold amount for **Shift**, operating before measurements are taken while the shutter is closed for **Bgavg**. A call of **Sigrun** followed by **Bands** yields a result with no light on the sample, so that the difference between the maximum and minimum values gives a measure of the noise amplitude. This is multiplied by an arbitrary factor of 1.6 to set the threshold.

Check For each array scan, as stored before any processing, this routine selects the count value at the pixel closest to the reflected wavelength. If this exceeds 65000, which is close to the saturation value for the array, a warning is given and the program is terminated. Without this precaution the largest signals could be truncated, causing an error. **Check** also examines the value in the band corresponding to the reflected wavelength after use of **Bands** and **Shift**. If this is less than the threshold value from **Shinit** a warning is given, as this could indicate that the illumination has failed or the monochromator has not stepped correctly.

Nonoise The use of this routine is optional. For each store containing a measurement, it sets the count equal to zero for places where the signal is not significantly above the noise level. Rather than simply using single values, it examines a small group of values centred on the place of interest, and sets zero if all values in the group are less than the threshold found by **Shinit**; this deals more effectively with regions where the signal is beginning to rise.

Deconv This routine is also optional. For the reflected light, the signal would ideally be confined to a single band. In practice a small proportion spreads symmetrically into adjacent bands; in fact the spread can be considerable if there is no slit at the spectrometer entrance and lateral diffusion of the light in the sample. If the effect is greater for the sample than for the reference white, it produces a negative imprint of the irregularities of the D_{65} daylight distribution function on the final plot of effective reflectance factor. **Deconv** carries out an elementary deconvolution process, subtracting a small proportion of the value in each band from its two neighbours and adding twice this amount to the band itself to keep the total constant. At present, the proportion to be used is set by the operator.

Compact After the use of **Bands**, each result is stored in only the first 93 of the 1024 available locations, and there are two sets of 93 stores containing results for sample and white, as this is the number of illumination wavelengths. It is convenient to have these results in stores 1 to 93 and 101 to 193, using the vacant stores from 94 to 100 and from 194 to 200 for standard tables and results of calculations. To make the permanent storage of results more efficient, **Compact** reduces the number of stores from 200 to 20. The results are treated as groups of ten, each group being copied to a single store, with successive results starting at locations 0, 100, 200, etc.

The **Bands**, **Shift** and **Check** routines operate on each spectrum immediately after it has been recorded without increasing significantly the overall measurement time. The spectrum is then scaled, using the appropriate entries in the monitor detector calibration tables and a table of standard D_{65} daylight, to obtain values corresponding to daylight illumination. Summation of these scaled spectra for all the incident wavelengths from 320 to 780 nm as a measurement sequence proceeds yields the total response of the array for the daylight illumination. The theory upon which the calculations are based is given in the Appendix.

The same procedure is used for the reference white as for the sample. Since the white only reflects at the incident wavelength, it is in principle possible to reject the values outside this wavelength region, which should only show random noise. However, measuring the reference white against itself using this procedure, before the introduction of **Nonoise**, gave a spectral reflectance which was slightly too high and showed a periodic variation with a periodicity of 20 nm. The source of this is difficult to identify, but it could be due to interference of the main beam with the secondary beam reflected at the surface of the array and then from the outer surface of the cover plate. The sample and reference are therefore now treated in the same way, which is sounder metrologically.

After measurements have been completed, the result for the sample is divided by the result for the reference white, corrected to correspond to a perfect diffuser, which yields the effective radiance factor of the sample for standard daylight. Because the diode array provides a complete spectrum of reflection and emission for each excitation wavelength, the theory as presented in the Appendix is more straightforward than that needed previously and correct results are obtained if more than one fluorophore is present. If colour data are required, the reflectance spectrum is multiplied by the normalized D_{65} distribution and the appropriate tabulated weighting functions.

7 SPECTROFLUORIMETER: RESULTS

As an example of the service now available, this section summarizes measurements made for a commercial customer. The samples examined were of orange-red and yellow fluorescent plastic materials used for safety clothing. The chromaticities and luminance factors were required to comply with the European standard EN 471: High Visibility Warning Clothing. The samples were not completely opaque, and were therefore backed with sheets of polished black perspex, which has a reflectance of less than 4% as required by the standard. Since the samples had the coarse surface structure mentioned earlier, the area illuminated was increased to 4 mm square.

Figure 2 shows a typical family of diode array scans for a series of illumination wavelengths, for the orange-red sample. Table 1 gives the final results from a series of measurements. For different measurements on each sample, the sample was rotated through a right angle in its own plane and the amount of defocus of Mirror 3 was altered, to change the proportion of the spectrometer aperture that was filled. The regions of the samples illuminated were randomly different between measurements. For each measurement, the table gives the values of chromaticity coordinates x and y and luminance factor β_v , required by the standard, and the derived quantities in CIELAB colour space. It also gives mean values, and the distances ΔE of the individual values from the mean point in the colour space.

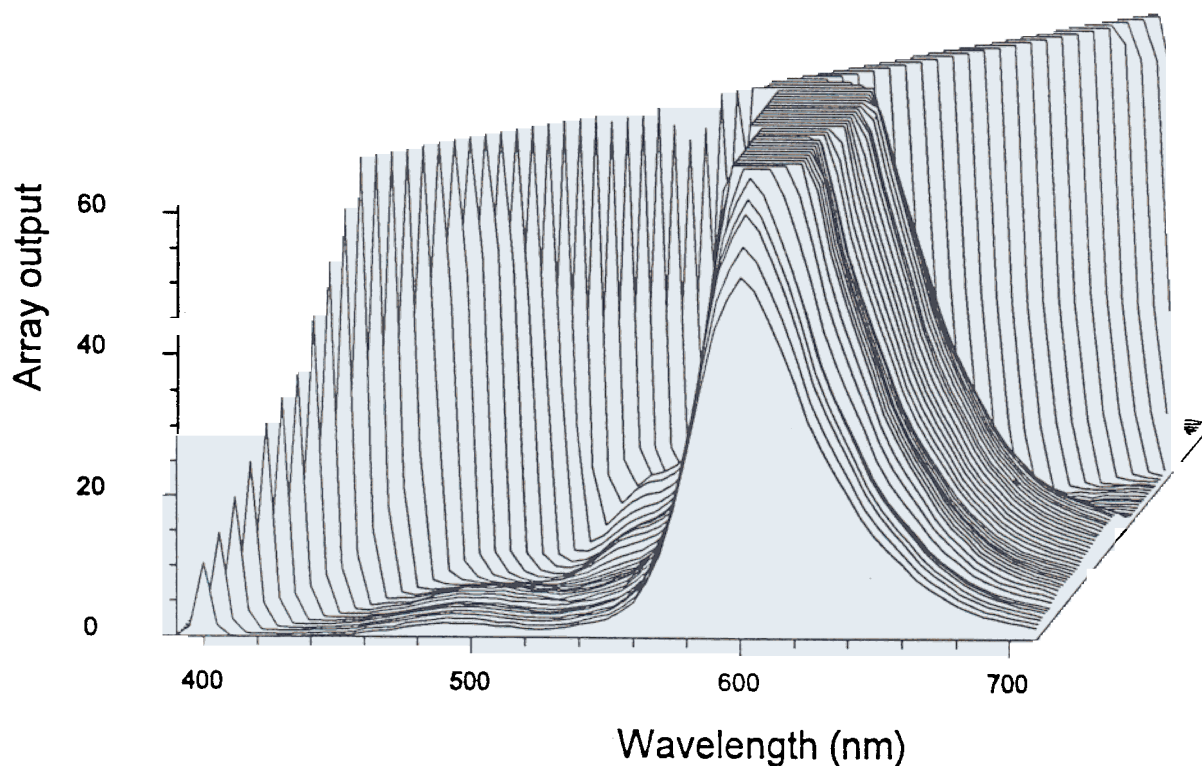


Figure 2 Set of diode array spectra for orange-red sample

Table 1 Results of measurements on fluorescent clothing materials

Orange-red sample							
	x	y	β_v	L^*	a^*	b^*	ΔE
	0.600	0.359	0.524	77.5	83.6	85.0	0.4
	0.598	0.359	0.531	77.9	83.2	84.9	0.9
	0.600	0.360	0.525	77.6	83.3	85.8	0.7
	0.601	0.359	0.522	77.4	83.7	85.9	0.7
	0.601	0.357	0.503	76.3	83.4	83.3	2.1
	0.604	0.359	0.506	76.4	83.6	86.7	1.6
Mean	0.601	0.359	0.520	77.2	83.5	85.3	
Std error	0.001	0.001	0.005	0.3	0.8	0.5	
Yellow sample							
	x	y	β_v	L^*	a^*	b^*	ΔE
	0.374	0.572	1.058	102.2	-59.8	113.6	1.8
	0.371	0.570	1.038	101.5	-59.8	110.1	2.0
	0.371	0.574	1.010	100.4	-60.4	111.7	1.1
	0.374	0.572	1.054	102.1	-59.7	113.6	1.8
	0.368	0.574	1.040	101.5	-62.4	110.8	2.3
Mean	0.371	0.572	1.040	101.5	-60.4	112.0	
Std error	0.001	0.001	0.008	0.3	0.5	0.7	

The values of β_v comfortably exceed those required by the standard, namely 0.40 for orange-red and 0.76 for yellow. Four of the eleven values of ΔE lie within the target accuracy of unity for the project; some of the variation in the others may be attributable to the small-scale nonuniformity of the samples. The uncertainty of the position of the mean point in CIELAB space is of the order of unity.

A principal source of systematic uncertainty is the uncertainty of 0.007 in the reflectance of the reference white. A change of this amount changes the values of L^* , a^* and b^* by 0.3, 0.2, 0.2 for the orange-red sample and 0.2, 0.2, 0.3 for the yellow sample.

8 SPECTROFLUORIMETER: CUSTOMER SERVICE

Calibrations of fluorescent samples, including whites such as paper and coloured materials giving high conspicuity, can now be undertaken on a routine basis and the presentation of the results can be tailored to suit customer needs. While the accuracy is adequate for many requirements, it could be improved further by more meticulous examination of the performance and by intercomparison with other instruments.

Calibrated transfer standards can also be provided, although their colours and stability characteristics are rather unsatisfactory. The development of improved materials is still a desirable goal.

APPENDIX

Spectrofluorimeter theory

When the the array signal for a particular illumination wavelength is processed, the counts from the individual array elements are first summed into bands which correspond to wavelength intervals of 5 nm. These bands are centred on wavelength values λ which correspond to the wavelength values μ to which the illumination is set. Suppose that the total count in a particular band is $c(\lambda, \mu)$ and that the current from the trap detector monitoring the illumination is $i(\mu)$. The optical power incident on the sample is then $i(\mu) / s(\mu)$, where the effective responsivity $s(\mu)$ includes an allowance for the ratio of the power reaching the sample to that reflected to the detector. Therefore the count value for unit incident power is $[s(\mu) / i(\mu)] c(\lambda, \mu)$.

Suppose now that the incident power corresponding to the standard illuminant of interest is $P(\mu)$. If it were possible to simulate this illuminant, the signal count in the band being considered would have been $P(\mu) [s(\mu) / i(\mu)] c(\lambda, \mu)$. To obtain the total count $C(\lambda)$ in the 5 nm interval if the sample receives all of the light from the illuminant simultaneously, the contributions due to the individual wavelengths are summed, so that

$$C(\lambda) = \sum P(\mu) [s(\mu) / i(\mu)] c(\lambda, \mu)$$

When the reference white is substituted for the sample, the total signal count $C_w(\lambda)$ in a 5 nm band corresponding to the standard illuminant is given similarly by

$$C_w(\lambda) = \sum P(\mu) [s(\mu) / i(\mu)] c_w(\lambda, \mu)$$

Ideally the summation would not be necessary in this case, as with no fluorescence each band only contains a signal when the illumination wavelength is that corresponding to it. However, the summation takes care of overspill into neighbouring bands in the same way as for the sample, which reduces systematic error.

The known spectral radiance factor $\beta_{ew}(\lambda)$ of the reference white can then be multiplied by the ratio of the total counts for sample and reference white to obtain the effective spectral radiance factor $\beta_e(\lambda)$ for the sample, corresponding to the standard illuminant. Thus

$$\beta_e(\lambda) = [C(\lambda) / C_w(\lambda)] \beta_{ew}(\lambda).$$

At this stage, colour data can be obtained in the usual way. The spectral radiance factor is multiplied by tabulated data for the illuminant $P(\lambda)$ and the colour matching functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$, and summation over the visible spectrum then yields tristimulus values X , Y and Z . Thus

$$Y = k \sum \bar{y}(\lambda) P(\lambda) \beta_e(\lambda)$$

where

$$k = 1 / \sum \bar{y}(\lambda) P(\lambda)$$

with similar equations for X and Z . If it were not necessary to allow for overspill of the reflected light, the factor $P(\lambda)$ in the above equation for Y could be cancelled with $P(\mu)$ in the equation for $C_w(\lambda)$. The chromaticity coordinate x is then given by

$$x = X / (X + Y + Z)$$

with a similar expression for y , and the factor k makes the luminance factor β_v equal to Y .

ADDENDUM

Recent developments

Since this Report was originally written, the illuminated area on the sample has been increased further, from about 4 mm square as described in Section 5.3 to about 15 mm square. This has enabled measurements to be made on samples which combine a fluorescent pigmentation with a coarse retroreflecting surface structure. The reduction in surface brightness has been compensated by increasing the illumination monochromator's exit slit height from 1.0 mm to 2.5 mm and its bandwidth from 0.5 nm to 5 nm. This bandwidth is now equal to the wavelength scan increment and the detection bandwidth. The increased size of the slit image in front of the sample is acceptable, as its ratio to the sample patch size remains about the same.

Further measures have been taken to increase the power detected by the diode array. A fused silica condenser lens has been placed in front of the xenon arc source, to increase the size of its image on the entrance slit of the illumination monochromator. The horizontal slit at the entrance to the array monochromator has been removed, so that the full height of each diode defines the collection geometry. To ensure that the trap detectors are still collecting the light completely, they are being replaced with a newer version having a larger acceptance aperture. The single planoconvex lenses imaging the light into them have been replaced by lens pairs to increase the aperture and reduce the aberration. These improvements have made the Reference Spectrofluorimeter better suited to customer requirements.

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