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**ABSOLUTE MEASUREMENT METHODS FOR  
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Doctoral Dissertation

**Silja Holopainen**



**Helsinki University of Technology  
Faculty of Electronics, Communications and Automation  
Department of Signal Processing and Acoustics**

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Doctoral Dissertation

**Silja Holopainen**

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Abstract			
<p>Reflectance and fluorescence are important properties when determining the colour and appearance of solid opaque material. They are also useful in several other industrial applications such as those in biochemical and medical industry and in remote sensing. In most industrial applications, the reflectance and / or fluorescence characteristics of samples are measured relative to a known reference standard. The uncertainty of the measurements is naturally dependent on the uncertainty of the reference standard and therefore it is vital to have high-accuracy calibration instruments capable of absolute measurements. In addition, the standards should be calibrated in the same measurement geometry as the application where they are used. Particularly, instruments capable of absolute fluorescence measurements commonly use a fixed measurement geometry and therefore there is a need for an instrument that does not have this limitation.</p> <p>In the thesis, goniometric measurement facilities for measuring reflectance and fluorescence characteristics of reference standards have been designed and developed. The significance of light scattering in goniometric diffuse reflectance measurements has been studied. The effect can cause errors of the order of 1 % in the measurements if it is not properly taken into account. Also, this effect may be at least partly responsible for the discrepancies reported earlier between goniometric and integrating-sphere-based diffuse reflectance measurements. The wavelength range of an existing gonioreflectometer for calibrating reflectance and radiance factors has been extended and an extensive bilateral comparison in the wavelength range 250 nm – 1650 nm is reported. Such extensive comparisons between goniometric instruments are very rare even though it is the only way to verify the reliability of the absolute scales in National Metrology Institutes.</p> <p>A goniofluorometer has been designed and developed for measuring bispectral luminescent radiance factors in various measurement geometries. Also, the theory and mathematics of a new method for measuring absolute fluorescence quantum yield based on goniometric measurements has been derived. One of the most significant results of this thesis is the discovery of non-Lambertian behaviour of fluorescence emission from solid amorphous material. In addition, it has been observed that the angular pattern of fluorescence emission is not very tightly linked to the angular pattern of reflectance. This is an important result since most commercial and research instruments are only capable of measurements in a fixed geometry and usually rely on the assumption of Lambertian emission of fluorescence.</p>			
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<p>Heijastus ja fluoresenssi ovat tärkeitä ominaisuuksia kiinteän läpinäkyvän materiaalin värin ja ulkonäön määrittämisessä. Niitä käytetään myös monilla muilla teollisuuden aloilla kuten esim. biokemian- ja lääketieteellisuuden sovelluksissa sekä kaukokartoituksessa. Useimmat sovellukset mittaavat heijastusta ja / tai fluoresenssia suhteessa referenssinormaalisiin. Näiden mittausten epävarmuus riippuu luonnollisesti referenssinormaalien epävarmuudesta ja sen vuoksi normaaleja kalibroivien laitteiden kehittäminen on ensiarvoisen tärkeää. Lisäksi normaalit tulisi kalibroida siinä mittaustilanteissa, jossa niitä käytetään. Kuitenkin erityisesti fluoresenssinormaalien kalibroivat laitteet pystyvät yleensä mittauksiin vain yhdessä geometriassa. Sen vuoksi on tärkeää kehittää laitteita, joilla ei ole tätä rajoitusta.</p> <p>Tässä väitöskirjassa on kehitetty uusia goniometriseen mittausten menetelmään perustuvia laitteita ja parannettu aiemmin kehitettyjä laitteita heijastus- ja fluoresenssimittauksia varten. Valon siroamisen merkitystä goniometrisissa hajaheijastusmittauksissa on tutkittu. Ilmiö voi aiheuttaa prosenttien suuruusluokkaa olevia virheitä, jos sitä ei huomioida mittaauksissa. Lisäksi tämä ilmiö saattaa olla ainakin osittain vastuussa aiemmin raportoiduista goniometristen ja integroivien pallojen perustuvien mittaustulosten välisistä eroista. Olemassaolevan gonioreflektometrin aallonpituusalueella on laajennettu ja kattavan kahdenvälisen vertailumittauksen tulokset aallonpituusvälillä 250 nm – 1650 nm on raportoitu tässä työssä. Näin laajat vertailut goniometristen laitteiden välillä ovat harvinaisia, vaikka ne ovat ainut tapa varmentaa absoluuttisten mittausten menetelmien oikeellisuus kansallisissa mittanormaali-laboratorioissa.</p> <p>Väitöskirjassa on kehitetty goniofluorometri bispektristen luminesenssi-radianssikerroimien mittaamiseen useissa mittaustilanteissa. Sen lisäksi on johdettu teoreettinen ja matemaattinen pohja uudelle goniometrisiin mittauksiin perustuvalla menetelmällä absoluuttisen fluoresenssin kvanttihyötysuhteen mittaamiseen. Yksi väitöskirjan merkittävimmistä tuloksista on fluoresenssimittauksissa tavallisesti käytetyn oletuksen kumoaminen fluoresenssiemission Lambertiaanisesta isotrooppisesta luonteesta kiinteissä amorfisissa aineissa. Lisäksi väitöskirjassa on osoitettu, että vastoin oletuksia fluoresenssiemission kulmariippuvuus ei ole läheisessä yhteydessä heijastuksen kulmariippuvuuteen. Tulos on merkittävä, sillä useimmat fluoresenssistandardeja kalibroivat laitteet pystyvät mittaamaan vain yhdessä geometriassa ja yleensä nojaavat oletukseen fluoresenssiemission Lambertiaanisesta luonteesta.</p>			
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## Preface

The research work of this thesis has been carried out at the Metrology Research Institute (MRI) in Helsinki University of Technology during 2004 – 2008 and at the Physikalisch-Technische Bundesanstalt (PTB) during 2008 – 2009. I wish to thank Professors Pekka Wallin and Erkki Ikonen for giving me the opportunity to work in the interesting field of optical metrology. Prof. Ikonen has provided invaluable guidance and encouragement during the work. I also wish to thank Prof. Fritz Riehle, Dr. Stefan Kück and Dr. Andreas Höpe for the opportunity to strengthen and widen my knowledge in the field of optical reflectometry at PTB.

I wish to express my gratitude to my instructor Dr. Farshid Manoocheri. His guidance and patience have been most valuable. I am grateful to all my co-authors and colleagues at the MRI and PTB. Special thanks go to Lic. Tech. Maija Ojanen for her help in practical matters concerning the thesis and above all for all the professional and non-professional discussions during this work.

The preliminary examiners Dr. Markku Hauta-Kasari and Dr. Joanne Zwinkels are highly appreciated for their efforts.

I am grateful for grants from the Foundation of Technology – TES, the Finnish Foundation for Economic and Technology Sciences – KAUTE, the TKK Committee for Research and Doctoral Education, and the Braunschweig International Graduate School of Metrology – IGSM.

Finally, I wish to thank my dear boyfriend and life companion Aleksi Ahtiainen and my parents for their love and support during my studies and the writing of the thesis.





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## List of Publications

This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.

- I** S. Holopainen, F. Manoocheri, S. Nevas and E. Ikonen, "Effect of light scattering from source optics in goniometric diffuse reflectance measurements", *Metrologia* **44**, 167-170 (2007).
- II** S. Holopainen, F. Manoocheri, E. Ikonen, K. O. Hauer and A. Höpe, "Comparison measurements of goniometric spectral diffuse reflectance and 0 : 45 radiance factors", *Applied Optics* **48**, 2947-2957 (2009).
- III** S. Holopainen, F. Manoocheri and E. Ikonen, "Goniofluorometer for characterization of fluorescent materials", *Applied Optics* **47**, 835-842 (2008); **47**, 6880 (2008).
- IV** S. Holopainen, F. Manoocheri and E. Ikonen, "Non-Lambertian behaviour of fluorescence emission from solid amorphous material", *Metrologia* **46** (2009), in press.



## **Author's contribution**

All publications included in this thesis are a result of team work of the authors.

The manuscripts of all publications were prepared by the author and the author has contributed to the design and realization of the work reported in all publications.

Part of the measurements of publications I and III were done by the author. All measurements of publication II at Helsinki University of Technology (TKK) and part of the measurements at Physikalisch-Technische Bundesanstalt (PTB) were performed by the author. All measurements of publication IV were carried out by the author.

The measurement data of publications I, III and IV were analyzed by the author. All measurement data from measurements at TKK and part of the measurement data from measurements at PTB for publication II were analyzed by the author.

The method for determining absolute fluorescence quantum yield which is derived in the appendix of publication IV was developed by the author.



# 1 Introduction

## 1.1 Background

The colour and appearance of any material is defined by three factors: the illuminating source, the object and the observer. If any of these three components changes, the observed colour changes.

A standard observer refers to an ideal colorimetric observer with colour-matching functions  $\bar{x}$ ,  $\bar{y}$ ,  $\bar{z}$  corresponding to a field of view subtending  $2^\circ$  (or  $10^\circ$ ) angle on the retina. The colour-matching functions are also tabulated for both  $2^\circ$  and  $10^\circ$  standard observers. A defined standard illuminant refers to specific tabulated values of spectral power distribution  $S(\lambda)$ . These standard illuminants try to define certain illumination conditions such as e.g. typical domestic illumination based on tungsten-filament lighting (illuminant A) or the daylight illumination (illuminant D65). [1–3]

When determining the surface colour of a solid opaque sample material, the most important object related property is the total radiance factor  $\beta_T(\lambda)$  of the material which defines the spectral composition of the light reflected and emitted by the sample. The total radiance factor is a sum of the reflection radiance factor and the fluorescence radiance factor, the latter being zero for all non-fluorescent materials. The reflection radiance factor is not sensitive to specific illumination conditions, but the fluorescence radiance factor for a fluorescent material depends critically on illumination. The actual light sources in practical measurement instruments differ from the standard illuminants. However, the fluorescence radiance factor can be derived for a specific illuminant from sample specific illumination independent bispectral luminescent radiance factor data. If an object's reflection radiance factors and bispectral luminescent radiance factors, namely the Donaldson radiance factors [4], are known, its colour properties can be calculated for any desired illumination and



observer.

Reflectance and fluorescence measurements and the appearance of objects are important in several applications such as e.g. paper industry [5] and remote sensing [6]. For example, the colour of normal copying paper is crucially dependent on fluorescence. A more comprehensive review of the applications of fluorescence is given in reference [7].

In order to determine the reflectance and fluorescence properties of a sample, most applications measure relative to a calibrated reference standard. The uncertainty of these measurements is naturally directly dependent on the uncertainty of the reference standard. Therefore, it is vitally important to have calibration facilities capable of more reliable absolute measurements.

The reflection radiance factor is well known to depend critically on measurement geometry i.e. the illumination and viewing angles. However, the bispectral luminescent radiance factor of solid amorphous fluorescence standards is often taken to be independent of the viewing angle. Furthermore, most instruments capable of measuring bispectral luminescent radiance factors can measure only in one measurement geometry and measurements of the bispectral luminescent radiance factor as a function of the viewing angle have not been published.

## **1.2 Contents of the thesis**

In this thesis calibration facilities for reflectance and fluorescence measurements are developed and tested. Chapter 2 presents the basic principles of reflectance measurements and an overview of the commonly used measurement methods. Then, the significance of light scattering from source optics in goniometric diffuse reflectance measurements is discussed (publication I). Also, the characterization of a gonioreflec-

tometer for measurements at ultraviolet and near infrared wavelengths and results of an extensive bilateral comparison are presented (publication II).

Chapter 3 first presents the basic principles of fluorescence as a physical phenomenon and shortly discusses the existing measurement methods. Then, a new kind of fluorometer capable of measuring in various measurement geometries is described (publication III). Measurement results obtained with this device are presented and a new method for measuring fluorescence quantum yield is introduced (publication IV).

The final chapter presents a short summary and the most important results of the work.

### **1.3 Scientific contribution**

This thesis contains the following new scientific results:

1. Light scattering from source optics in goniometric diffuse reflectance measurements can have a significant effect on the measurement results. Also, this phenomenon may be partly responsible for the differences reported earlier between goniometric and integrating-sphere-based diffuse reflectance scales.
2. One of the first reported comparisons of diffuse reflectance and bidirectional radiance factor scales using goniometric methods over an extended wavelength range
3. A new goniofluorometer has been developed capable of measuring bispectral luminescent radiance factors in various measurement geometries.
4. The common assumption of Lambertian behaviour of fluorescence emission from solid amorphous material has been studied and, surprisingly, found not

to hold.

5. The theory and mathematics of a new method for measuring fluorescence quantum yield based on goniometric measurements has been derived. This method is not prone to the problems related to methods based on integrating spheres; namely sphere wall contamination leading to reduced throughput / fluorescence in the UV-region and re-reflection of emitted light from the sphere wall leading to re-absorption and distortion of the emission spectrum.

## 2 Reflectance

### 2.1 General theory

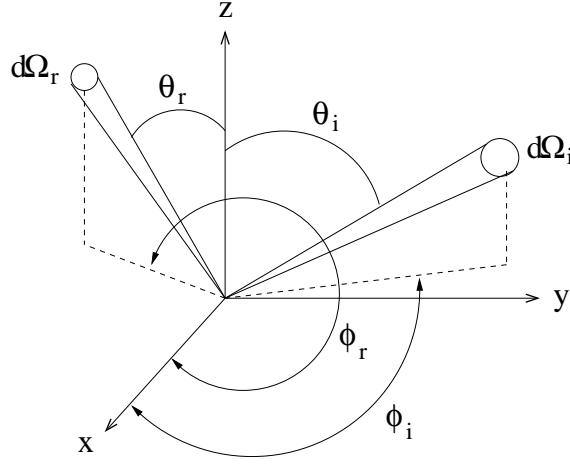
In most applications that utilize reflectance measurements, the reflectance of a sample is measured relative to a known reflectance standard. For this reason, it is important to have reliable calibration facilities capable of measuring these standards in absolute means.

Under uniform irradiance the geometrical reflectance properties of a uniform, isotropic, flat surface are characterized in terms of the bidirectional reflectance distribution function (BRDF). The BRDF is defined by [8]

$$f_r(\theta_i, \phi_i, \theta_r, \phi_r) = \frac{dL_r(\theta_i, \phi_i, \theta_r, \phi_r, E_i)}{dE_i(\theta_i, \phi_i)} = \frac{dL_r(\theta_i, \phi_i, \theta_r, \phi_r, E_i)}{L_i(\theta_i, \phi_i) \cdot \cos \theta_i \cdot d\Omega_i}, \quad (2.1)$$

where  $dL_r$  is the differential radiance of the surface in direction  $(\theta_r, \phi_r)$  when irradiated by irradiance  $dE_i$  from direction  $(\theta_i, \phi_i)$ , and  $L_i$  is the total irradiating radiance over a differential incident solid angle  $d\Omega_i$ . The directions and solid angles are illustrated in figure 2.1.

Reflectance standards are usually made to resemble Lambertian radiators as closely as possible. These kinds of standards are commonly characterized by their reflectance factor. The reflectance factor is defined as the ratio of the flux reflected by the sample in a given direction to the flux reflected by a perfect reflecting diffuser (prd) identically irradiated and viewed. A prd reflects all light incident upon it like a perfect Lambertian radiator. No real material has the exact properties of a prd. For reflectance factors, the solid angle of viewing is defined in the interval  $]0, 2\pi[$ . When



**Figure 2.1:** Geometry of the incident and reflected radiation. The sample surface is parallel to the x-y-plane.

the solid angle approaches 0 or  $2\pi$  the reflectance factor approaches the radiance factor or reflectance, respectively. [9]

Reflectance is also commonly referred to as the hemispherical reflectance factor and it can be calculated from measurements of radiant flux over polar angles assuming cylindrical symmetry. That is, the radiant flux reflected by the sample is only a function of  $\theta_r$  and independent of  $\phi_r$  (see figure 2.1). The flux reflected over a solid angle  $\Omega$  can be given by

$$\Phi_r = \int_{\Omega} \Phi'_r(\theta) d\Omega = \int_{\phi_1}^{\phi_2} \int_{\theta_1}^{\theta_2} \Phi'_r(\theta) \sin \theta d\theta d\phi = (\phi_2 - \phi_1) \int_{\theta_1}^{\theta_2} \Phi'_r(\theta) \sin \theta d\theta, \quad (2.2)$$

where  $\Phi'_r(\theta)$  is the flux per unit solid angle reflected in direction  $\theta$  and  $\Omega$  is the solid angle of detection (reflection). For a prd we can write  $\Phi_{\text{prd}}(\theta) = \Phi_0 \cos \theta$ , where  $\Phi_0$  is the flux reflected in the direction of the sample normal ( $z$ -direction in figure 2.1). Inserting this into equation 2.2 gives for the flux reflected by a prd

$$\Phi_{r,prd} = (\phi_2 - \phi_1) \int_{\theta_1}^{\theta_2} \Phi_0 \cos \theta \sin(\theta) d\theta = \frac{\phi_2 - \phi_1}{2\pi} \int_{\theta_1}^{\theta_2} \Phi_i \sin(2\theta) d\theta, \quad (2.3)$$

where  $\Phi_i$  is the flux incident on the sample and  $\Phi_i = \pi\Phi_0$ . The flux reflected by the sample under measurement,  $\Phi_{r,s}$ , can be derived from equation 2.2 by [10]

$$\begin{aligned} \Phi_{r,s} &= (\phi_2 - \phi_1) \int_{\theta_1}^{\theta_2} \frac{\Phi(\theta)}{\pi(\frac{1}{2}D)^2/L^2} \sin \theta d\theta \\ &= \frac{\phi_2 - \phi_1}{2\pi} \int_{\theta_1}^{\theta_2} \Phi(\theta) \frac{4L^2}{D^2 \cos \theta} \sin(2\theta) d\theta, \end{aligned} \quad (2.4)$$

where  $\Phi(\theta)$  is the flux reflected by the sample in direction  $\theta$  over a solid angle defined by an aperture of diameter  $D$  at distance  $L$  from the sample. The reflectance factor,  $R_\Omega$ , in solid angle  $\Omega$  can be derived by dividing equation 2.4 by equation 2.3

$$R_\Omega = \frac{\Phi_{r,s}}{\Phi_{r,prd}} = \frac{\int_{\theta_1}^{\theta_2} \beta(\theta) \sin(2\theta) d\theta}{\int_{\theta_1}^{\theta_2} \sin(2\theta) d\theta}, \quad (2.5)$$

where  $\beta(\theta)$  is the radiance factor

$$\beta(\theta) = \frac{\Phi(\theta)}{\Phi_i} \frac{4L^2}{D^2 \cos \theta}. \quad (2.6)$$

In equation 2.6 the distance  $L$  must be sufficiently large and the diameter  $D$  sufficiently small so that the corresponding solid angle is close to zero. If the integration in equation 2.5 is carried out over the hemisphere ( $\theta_1 = 0$  and  $\theta_2 = \pi/2$ ) the denominator in the equation becomes one and the reflectance factor becomes the hemispherical reflectance factor. If the specular component is excluded, the reflectance

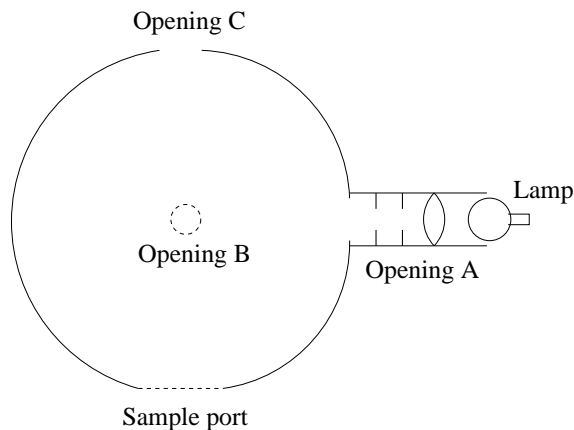
factor becomes the diffuse reflectance factor. Reflectance standards are commonly characterized by the diffuse reflectance factor.

## 2.2 Reflectance measurements

An overview of absolute methods for reflectance measurements is given in reference [11]. Today, the most common methods used in the National Metrology Institutes (NMI) are the methods based on the theory of the integrating sphere and the goniophotometric method.

The theory of the integrating sphere states that, if the inner surface of the sphere is made of a uniformly diffusing material having a constant reflectance everywhere, the indirect illuminance caused by the reflected light is equal at all points on the surface no matter how the wall of the sphere or any point of it is directly illuminated [11]. This theory has been applied since the beginning of the 20th century. Particularly in 1920, several papers were published [12–14] describing methods based on the integrating sphere that have been since then actively used and modified.

As an example of integrating sphere based methods, figure 2.2 illustrates a method described in reference [13], namely the Taylor’s method. In this method, the sphere has three small openings A, B and C at about  $90^\circ$  angles relative to each other and a sample port opposite to opening C. The illuminating lamp is placed at opening A and a detector alternatively at opening B or C. During the measurements, the sample port is covered sequentially by I) nothing or a non-reflecting plate, II) a plate of the same material as the rest of the sphere wall and III) the sample. In the absolute method, light is incident on the wall opposite to opening A and the indirect reflection of the sphere wall is measured at opening B. The sphere wall reflectance is measured by comparing the signals between I) and II) after which the sample reflectance is derived by comparing I) and III).



**Figure 2.2:** Taylor's method based on the theory of the integrating sphere.

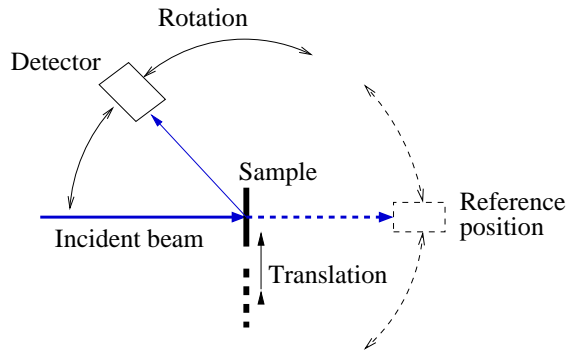
During the decades after 1920, the integrating sphere methods have been expanded and modified [15, 16]. Today, integrating-sphere-based absolute methods for measuring reflectance are widely used in many laboratories [16–21].

Goniophotometric methods have been gaining popularity in the NMIs only during the last couple of decades although they have been somewhat utilized already before the 1990s [22]. The advantage of gonireflectometers over integrating spheres is the ability to measure not only diffuse reflectance factors but also radiance factors in various bidirectional measurement geometries. Several NMIs have developed a gonireflectometer for calibration services and research [10, 23–26].

The basic idea of the gonireflectometer is illustrated in figure 2.3 which presents the gonireflectometer developed at the Helsinki University of Technology (TKK) [10]. The device employs two optional light sources, a xenon lamp for UV measurements and a quartz-tungsten-halogen lamp for VIS and NIR, and a double monochromator for wavelength selection. The light is collimated by an off-axis parabolic mirror and steered towards the sample by a flat mirror. A small part of the beam is directed onto a monitor detector which is used to compensate for possible fluctuations in



the incident beam power. The sample holder is placed on a linear translator that is used to move the sample into the beam path and out of the way so that the full intensity of the illuminating beam can be measured at the reference position. The detector is mounted on a cantilever which lies on a turntable that is used to rotate the detector over the polar angles around the sample. Reflectance is measured from  $10^\circ$  viewing angle relative to the incident beam to  $85^\circ$  in  $5^\circ$  step. Radiance factors are calculated for each measurement angle by equation 2.6 and the rest of the radiance factors needed for diffuse reflectance calculation by equation 2.5 are interpolated and extrapolated.



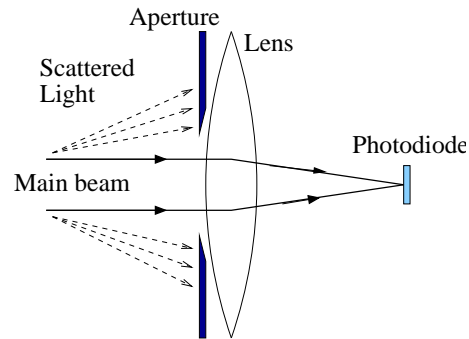
**Figure 2.3:** The gonioreflectometer at TKK.

The gonioreflectometers described in references [23–25] are basically similar to the one in reference [10]. However, the goniometric measurement facility in reference [26] is slightly different although the basic principle of integration over the hemisphere is always the same. The most distinguishing features in the PTB (Physikalisch-Technische Bundesanstalt) gonioreflectometer [26] are the sample holder and illumination. In the PTB measurement facility, the sample holder is a five-axis robot arm which provides the necessary illumination and viewing angles together with a sphere radiator mounted on a large rotation stage (diameter 1.5 m), and the detection side is fixed. Whereas at NIST (National Institute of Standards and Technology) [23,25], NPL (National Physical Laboratory) [24] and TKK [10] the detector is rotated in order to measure the polar angles around the sample. Also, the PTB gonioreflec-

tometer utilizes broadband irradiation and the wavelength selection is provided in the detection side by a monochromator. Both, the new NIST gonireflectometer [25] and the PTB gonireflectometer [26] have the ability to measure also in out-of-plane configurations.

In the NIST, NPL and TKK measurements, the radiant beam incident on the sample is shaped (focused or collimated) and when measuring full intensity all of the beam incident on the sample is measured. Also, when measuring reflectance the detector views all of the illuminated area of the sample. In the PTB system, the incident beam is not shaped after it emerges from the sphere radiator, but the sample is completely illuminated and the reflected light is measured from a well defined area on the sample. These different kinds of beam geometry and propagation set different demands on the illuminating beam quality. In the PTB setup, it is very important that the illuminating light is spatially homogenous which is evoked by the sphere radiator. On the other hand, in measurement facilities employing a shaped measurement beam, light scattering around the irradiating beam may cause significant problems as described in publication I. Figure 2.4 illustrates the situation when the light incident on the sample is collimated and the full intensity is measured somewhere behind the sample like in the gonireflectometer in figure 2.3. If the light is scattering from the optical components of the measurement system, all of the light that is incident on the sample at the sample position does not reach the detector at the reference position (see figure 2.3). This effect can be taken into account by determining a correction factor that tells how much light is missed by the detector at each wavelength. Methods to determine this correction factor are discussed in publication I.

Figure 2.5 presents the correction factors determined for the gonireflectometer described in reference [10] and in publications I and II. The figure presents correction factors measured in 2004 and 2007. In the 2004 measurements, a different monochromator suffering from astigmatism problems was used. The monochromator used in

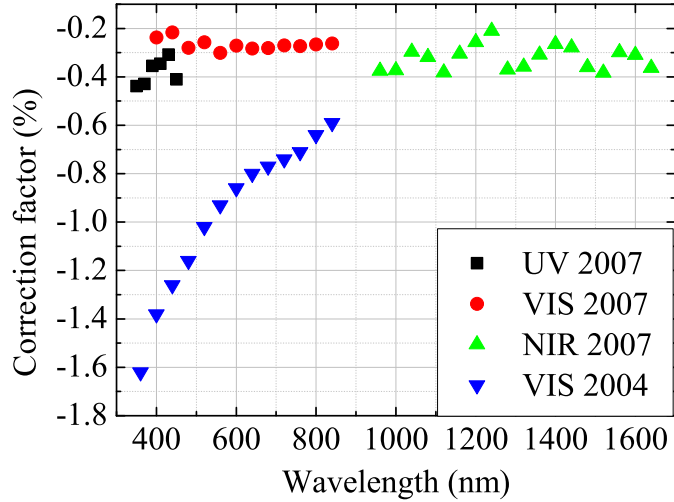


**Figure 2.4:** Light scattering around a collimated main beam.

2007 is astigmatism-free. Depending on the scattering properties of the source system, the correction factor can be as large as 1.6 % as illustrated in figure 2.5 and in publication I. The possibility of such a large error in the measured full intensity signal can not be neglected. Although light scattering from source optics can induce errors also in integrating sphere measurements when applying directional illumination, this kind of error, namely the "dark-sample reading error", has been long known and can be easily corrected [27]. Therefore, this effect may be at least partly responsible for the differences reported earlier between goniometric and integrating sphere based measurement techniques [28].

### 2.3 International comparison measurements

The verification of the absolute reflectance scales at National Metrology Institutes is commonly performed through international comparison measurements [29–31]. Within the last four decades, there have not been many reported comparisons of absolute reflectance scales realized by goniometric means [32, 33] and even fewer comparisons covering a wide wavelength range from ultraviolet to near infrared region.



**Figure 2.5:** The correction factor due to light scatter measured for the ultraviolet, visible and near infrared spectral regions.

Publication II presents the characterization of the gonireflectometer described in reference [10] and publication I for the UV and NIR regions and the results of an extensive bilateral comparison between this instrument and the PTB gonireflectometer [26, 34, 35]. The comparison was performed for  $0 : 45$  geometry in the wavelength range of 250 nm – 1650 nm in 10 nm interval and in the  $0 : d$  geometry in the wavelength range of 400 nm – 1600 nm in 100 nm interval. Altogether six different samples were measured. The samples and their nominal reflectances for the visible spectral range are presented in table 2.1.

The characterization of the TKK gonireflectometer for UV and NIR measurements was done similarly to the characterization for the visible range [10]. For UV measurements, a 450 W Xenon arc lamp was installed to the measurement system and an InGaAs detector was characterized for measurements in the NIR. Also, the Si detector and the amplifier were changed from those described in [10] be-

**Table 2.1:** The samples measured in the bilateral comparison between TKK and PTB.

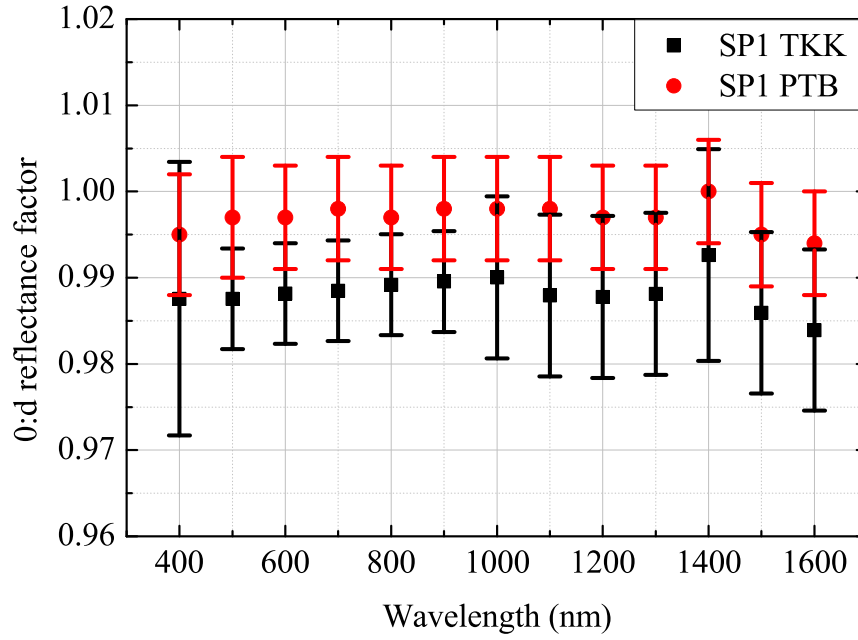
Sample name	Sample material	Nominal reflectance (%)
SP1	Spectralon	99
SRS1	Sintered PTFE	99
GO2	OP.DI.MA	98
OG1	Opal glass	96
RO1	Russian opal glass	96
CERAM#39	Ceramic tile	50

cause of the malfunction of the previous devices. The silicon detector is used for measurements between 250 nm – 1100 nm and the InGaAs detector is employed between 950 nm – 1650 nm. The Xenon lamp is used for irradiation between 250 nm – 450 nm and a 50 W halogen-tungsten lamp is employed above 400 nm in order to avoid the sharp peaks occurring in the Xenon power distribution above 450 nm [36]. An uncertainty budget is presented in publication II. All uncertainties have been evaluated according to reference [37].

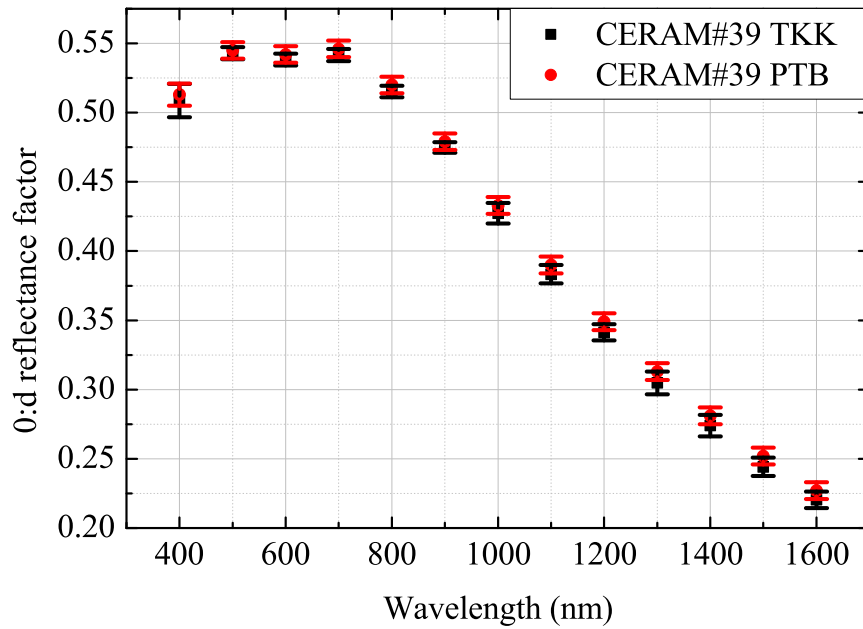
Figures 2.6 (a) and 2.6 (b) present the 0 : d diffuse reflectance factors measured at TKK and PTB for samples SP1 and CERAM#39, respectively. The error bars indicate expanded uncertainty with coverage factor  $k = 2$ . The figures show a good correspondence between the TKK and PTB results. Apart from a few measurement points, this is true for all sample measurements, but OG1, as can be seen in publication II. For OG1, the differences in the visible region and below 300 nm are outside the measurement uncertainties.

For all samples, the differences increase in the VIS-NIR transition region and for all

(a)



(b)



**Figure 2.6:** 0 : d reflectance factors measured at TKK and PTB for (a) SP1 and (b) CERAM#39. The error bars represent the  $k = 2$  uncertainties of the measurement results.

samples but the ceramic tile CERAM#39 the differences increase with increasing wavelength in the NIR region. The sudden increase in the differences measured at TKK and PTB in the VIS-NIR transition region is related to the amplifier gains used in the TKK measurement facility and the smaller size of the InGaAs diode (5 mm) compared to the Si diode (10 mm). The gains are different for the Si and InGaAs detectors and the associated uncertainties can cause a discontinuity between the VIS and NIR regions. Also, because of the small size of the InGaAs diode a relatively small size of the sample is viewed by the detector, thus making the measurements very sensitive to alignment. A slight misalignment may cause the InGaAs diode to miss a part of the illuminated area on the sample and thus underestimate the measured reflectance. The wavelength dependence of the differences is related to sample translucency and its different effect in the different measurement facilities of TKK and PTB as explained in publication II. The effect of translucency was investigated by measuring 45 : 0 radiance factors in the PTB gonireflectometer with and without a black non-reflecting aperture on the sample surface. The purpose of the aperture was to block the incident irradiation outside the measurement area on the sample and thus eliminate the effect of subsurface scatter into the measurement area as explained in publication II. A correction due to translucency was calculated for the strongly translucent samples RO1 and OG1 and the correction was applied to the 0 : 45 measurement results of these samples in the NIR range. At 1650 nm, the magnitude of the translucency correction for OG1 was 0.016.

The radiance factor measurements down to 250 nm show that below 310 nm the TKK values tend to rise relative to the PTB results. Below 300 nm isochromatic stray light at the TKK facility and low signal-to-noise ratio in the UV region are partly responsible for the effect. The correction for isochromatic stray light, discussed in publication I, has been evaluated only down to 300 nm. At shorter wavelengths it has been impossible to measure because of low signal-to-noise ratio. Other possible causes for the phenomenon in UV are fluorescence from the samples, wavelength accuracy and bandpass difference between the two facilities as explained in

publication II. Because TKK uses monochromatic irradiation and polychromatic detection and PTB employs polychromatic irradiation and monochromatic detection, fluorescence would not show in the PTB results at the short wavelengths but would be present in the TKK results increasing the measured radiance factor in the UV range. Fluorescence is a probable contributing factor in the case of the opal glass samples RO1 and OG1 and the ceramic tile CERAM#39, since for these samples fluorescence has been visibly observed when irradiated with intense short UV radiation at 254 nm from a mercury lamp. Also, earlier studies of photoluminescence of two different types of Russian Opal glass samples [38] and BCR opal glass standards [39] support this argument as explained in more detail in publication II.

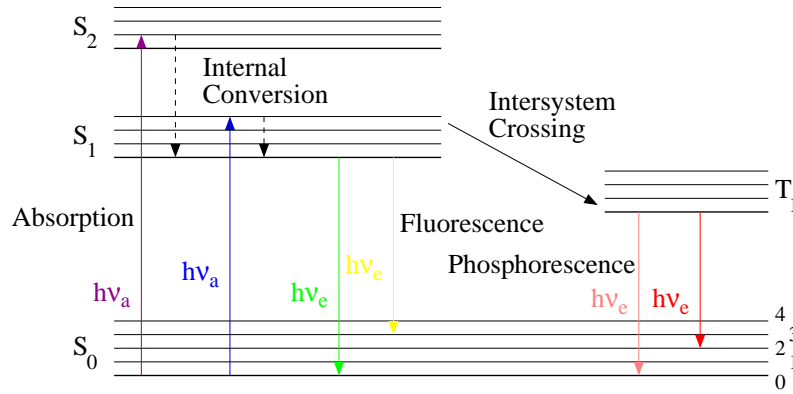


## 3 Fluorescence

### 3.1 General theory

Reflectance measurements are insufficient when determining the colour and appearance of luminescent samples. When light is incident on non-luminescent material part of the light is absorbed, part of it may be transmitted and the rest is reflected with the same wavelength. When illuminating a luminescent material, part of the absorbed light excites electrons in the sample from the ground state to higher energy states. The ground state and the other energy states are divided into vibrational states as depicted in figure 3.1 by a Jablonski diagram [40]. The ground state is denoted by  $S_0$  and the higher energy states are denoted by  $S_1$ ,  $S_2$ , and so on. The vibrational levels are denoted by 1, 2, 3, etc. Before returning back to the ground state, the electrons undergo internal conversions in the form of heat emission or collisions and are usually relaxed to the lowest vibrational levels of the first excited state  $S_1$ . From there they often return to some of the higher vibrational levels of the ground state  $S_0$  by emitting a photon of longer wavelength than the exciting photon. [41] The change in wavelength is denoted by Stokes shift [42] and the phenomenon is called fluorescence. The fluorescence life times (the time from excitation to the higher energy state to the relaxing back to the ground state) are typically between  $10^{-9} - 10^{-4}$  s [43].

Instead of internal conversions, the electron may undergo intersystem crossing by changing its spin and thus going to a triplet state which is denoted by  $T_1$  in figure 3.1. As fermions, two electrons can not exist in the same quantum mechanical energy state and thus the electron must change its spin before it can return back to the ground state. This procedure takes more time than the straightforward relaxing through the singlet states. The phenomenon is called phosphorescence and its life



**Figure 3.1:** A Jablonski diagram.  $S_0$ ,  $S_1$  and  $S_2$  denote singlet energy states (no change in electron spin) and  $T_1$  denotes a triplet state where the electron spin has changed. The solid vertical lines indicate photon absorption and emission and the dashed lines indicate internal conversions. The letter  $h$  indicates Planck’s constant and  $\nu_a$  ( $\nu_e$ ) is the frequency of the absorbed (emitted) photon.

time is typically between  $10^{-4} - 10$  s, but can in some cases be even hours [43]. The triplet states commonly have lower energy than the lowest excited singlet state and therefore phosphorescence usually occurs at longer wavelengths than fluorescence. Because the following discussion is limited to applications employing steady-state illumination and therefore it is not possible to discern between the different life times of fluorescence and phosphorescence, from here on the term fluorescence is taken to refer to both fluorescence and phosphorescence unless otherwise indicated. Also, the discussion is limited to opaque reflecting luminescent samples.

The reflectance of a fluorescent sample can not be determined in the same way as the reflectance of a non-fluorescent material like e.g. the reflectance measurements described in reference [10]. If a fluorescent sample is illuminated with monochromatic radiation and the reflectance is detected polychromatically, the reflectance values in the excitation range of the sample are increased because they include the emitted radiation occurring on longer wavelengths. This effect is illustrated for example in reference [44]. If the sample is illuminated polychromatically and reflectance is

detected monochromatically, the fluorescence does not disturb the reflectance values in the excitation range. However, the contribution of emission is added in the reflectance values in the emission range and it is impossible to discern which part is pure reflectance and which is fluorescence. Moreover, contrary to non-fluorescent material the total radiance factors for fluorescent samples are source dependent and therefore it is vital to be able to discern between reflectance and fluorescence.

The total radiance factor of a fluorescent sample,  $\beta_T$ , is a combination of the reflected radiance factor,  $\beta_R$ , and the fluorescence radiance factor,  $\beta_F$ , according to equation 3.1

$$\beta_T(\lambda, \theta) = \beta_R(\lambda, \theta) + \beta_F(\lambda, \theta), \quad (3.1)$$

where  $\lambda$  is the wavelength and  $\theta$  is the angle of detection. Parameter  $\beta_F$  is source dependent and it can be calculated for a given light source from the source independent bispectral luminescent radiance factors  $\beta_{L\mu}(\lambda, \theta)$  by integrating over all excitation wavelengths  $\mu$  giving emission at  $\lambda$  and weighting by the relative spectral power distribution of the source at excitation wavelength  $\mu$  and emission wavelength  $\lambda$

$$\beta_F(\lambda, \theta) = \int \frac{E_s(\mu)}{E_s(\lambda)} \beta_{L\mu}(\lambda, \theta) d\mu, \quad (3.2)$$

where  $E_s(\mu)$  and  $E_s(\lambda)$  are the relative spectral power distributions of the source at  $\mu$  and  $\lambda$ , respectively. The bispectral luminescent radiance factor is defined as the ratio of the emitted radiance from the sample per unit wavelength interval at  $\lambda$  due to excitation at  $\mu$  to the radiance of a perfect reflecting diffuser similarly irradiated and viewed. The total bispectral radiance factor is the sum of the bispectral luminescent radiance factor and the bispectral reflected radiance factor. The colour of a sample

for a defined illuminant and observer can be calculated from the total bispectral radiance factor.

Fluorescent pigments are widely used for example in paper, textile and plastic industry to brighten the colour or whiteness of products. In order to know exactly how much of a certain pigment should be used to produce the desired effect on the colour of a sample, it is helpful to know the fluorescence quantum yield of the pigment. The fluorescence quantum yield,  $Q$ , is defined by

$$Q = \frac{\text{The number of emitted photons}}{\text{The number of absorbed photons}} = \frac{n_e(\mu)}{n_a(\mu)}, \quad (3.3)$$

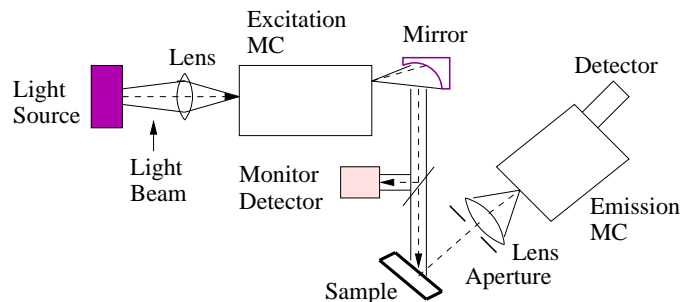
where  $n_e(\mu)$  is the total number of photons emitted when irradiated at wavelength  $\mu$ . The fluorescence quantum yield of a fluorophor is dependent on its environment and therefore it is usually measured for a specific standard or a solvent-solute-pair.

## 3.2 Fluorescence measurements

There are two commonly used basic methods for measuring fluorescence emission: the one-monochromator method and the two-monochromator method. In the one-monochromator method, the sample is illuminated by polychromatic radiation and the emitted signal is detected monochromatically whereas in the two-monochromator method both the radiation incident on the sample and the radiation emitted by the sample are determined monochromatically. It is possible, in principle with either method, to measure accurately the total radiance factor of a sample. However, since the fluorescent part of the total radiance factor is source dependent the total radiance factor will always be dependent on the source used with the one-monochromator method. The source independent bispectral luminescent radiance factors are possible to measure only with the two-monochromator method.

Although the two-monochromator method was introduced already in 1954 [4] the one-monochromator method is still much more widely used. The current status of the standardization of surface fluorescence (solid samples) measurements for colorimetric applications is discussed in more detail in reference [45].

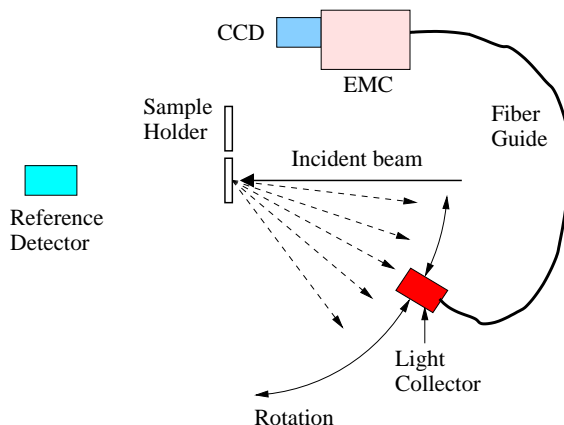
In practical measurements of fluorescence, as with reflectance, the measurements are made using a known reference standard. These fluorescence standards, in turn, are calibrated absolutely using reference instruments based upon the two-monochromator method. Most instruments capable of absolute measurements use a fixed measurement geometry [46–48]. The recommended measurement geometries in colour measurements are  $0 : 45$ ,  $45 : 0$ ,  $0 : d$  and  $d : 0$  or  $0 : t$  and  $t : 0$  [3]. Figure 3.2 presents the basic idea of a fluorometer using the two-monochromator method and  $45 : 0$  geometry.



**Figure 3.2:** The basic components in a fluorometer applying the two-monochromator method. MC stands for monochromator. Monitor detector can be used for recording the incident beam power.

Fluorescence standards should be calibrated in the same measurement geometry as the application where they are used and therefore it is important to have a measurement facility capable of calibrating fluorescence standards in various geometries. This kind of instrument, the goniofluorometer, is described in detail in publication III. The basic principle of the measurement facility is presented in figure 3.3. The instrument is meant for calibrating solid fluorescence standards. A

similar instrument has been built at the National Physical Laboratory (NPL) [49]. Also, a very versatile measurement device, "The Universal Spectrophotometer", capable in e.g. goniometric fluorescence measurements has been previously designed by a commercial company [50]. However, to my knowledge, no measurement results by such an instrument have been reported before publications III and IV.



**Figure 3.3:** The goniofluorometer. EMC stands for emission monochromator.

The emitted and reflected light is collected by a light collector comprising an aperture and a lens which focuses the light into a fibre guide. The fibre guide takes the light into the emission spectrometer comprising a monochromator (EMC) and a CCD detector. The core element of the system is a turntable [51] whose axis coincides with the sample surface. The light guide is mounted on a cantilever which lies on the turntable. The turntable provides viewing angles from  $10^\circ$  to  $90^\circ$  relative to the incident beam and the incident radiation is near normal.

Because in fluorescence measurements signals of different wavelength are compared to each other, it is essential to calibrate the instrument for emission system responsivity. Four different approaches for the spectral responsivity calibration of a fluorometer are listed in reference [3]. The goniofluorometer presented in publication III has been calibrated using the recommended method. This method employs

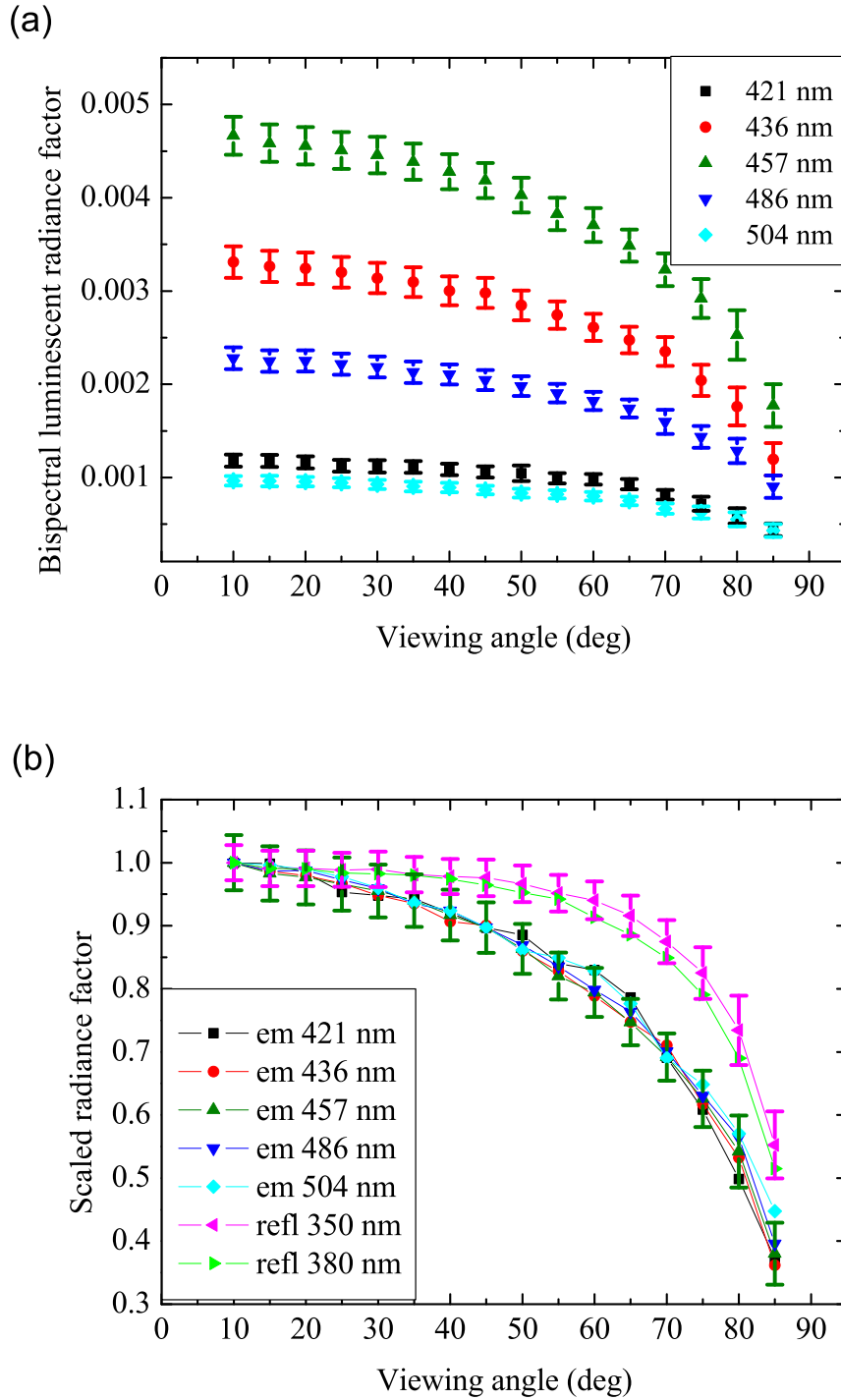
a calibrated non-fluorescent reflectance standard and a calibrated detector. The calibrated detector is referred to as the reference detector in figure 3.3.

### 3.2.1 Angular behaviour of fluorescence emission

Fluorescence emission from liquids and solid amorphous materials is commonly assumed to be Lambertian [43]. Fluorescence emission from solid crystalline materials has been studied extensively as a function of angle and polarization in order to determine the orientation of the fluorophores [52–55]. Understandably, the emission from crystals is not Lambertian because the fluorophores coated on crystal substrates have a defined orientation leading to angle dependent emission. On the other hand, in amorphous material the fluorophor orientation would be expected to be random and therefore the emission would also be Lambertian. However, this has hardly been studied at all although many times fluorescence measurements from amorphous samples rely on the assumption of Lambertian emission

The goniofluorometer described in publication III has made it possible to test the assumption of Lambertian emission from solid amorphous material. Figure 3.4 shows the angular behaviour of fluorescence emission from a Spectralon fluorescence standard [56] as discussed in publication IV. Figure 3.4 (a) presents bispectral luminescent radiance factors measured for emission wavelengths 421 nm, 436 nm, 457 nm, 486 nm and 504 nm as a function of viewing angle and figure 3.4 (b) depicts the same bispectral luminescent radiance factors and reflection radiance factors at wavelengths 350 nm and 380 nm scaled to unity at 10° viewing angle. The excitation wavelength is 350 nm and the incident irradiation is near normal. Emission at 457 nm is close to the emission maximum. The error bars correspond to expanded uncertainty with coverage factor  $k = 2$ .

It can be seen clearly from both figures 3.4 (a) and 3.4 (b) that the fluorescence emis-



**Figure 3.4:** (a) Bispectral luminescent radiance factors for emission wavelengths 421 nm, 436 nm, 457 nm, 486 nm and 504 nm at excitation wavelength 350 nm and (b) the same bispectral luminescent radiance factors and reflection radiance factors at 350 nm and 380 nm scaled to unity at a viewing angle of  $10^\circ$ .



sion is not Lambertian. If it were Lambertian the bispectral luminescent radiance factors would be constant with respect to the viewing angle. Moreover, figure 3.4 (b) shows that the angular pattern of fluorescence emission differs from the angular pattern of reflection even though the pattern is, within uncertainties, the same for all emission wavelengths. This is an important result concerning colorimetric measurements, since it shows that the measurement geometry plays a very important role when determining fluorescence radiance factors. In addition, it suggests that the fluorophor orientation in the sample may not be as random as would be expected for amorphous material even though figure 3.4 (b) shows that the reflection is very close to Lambertian up to  $\sim 60^\circ$ .

### 3.2.2 Fluorescence quantum yield measurements

Apart from the corrected spectral emission and excitation curves, two other important characteristics of a fluorophor are the fluorescence quantum yield and lifetime. The fluorescence lifetime is defined by the average time the electron spends in the excited state prior to return to the ground state. Both fluorescence quantum yield and lifetime depend on the radiative and non-radiative decay rates of the fluorophor. The greater the radiative decay rate is relative to the non-radiative decay rate the larger the quantum yield. Larger quantum yield means brighter emission. It is useful to know the fluorescence quantum yield of a fluorophor in order to estimate how much of the fluorophor is needed to produce desired emission. In the following, the discussion concerns solids. Liquid solutions are not discussed.

Most fluorometers that measure fluorescence quantum yield measure relative to a known fluorescence standard [57–59]. The uncertainty of the relative measurements is proportional to the uncertainty of the standard and therefore it is important to have calibration facilities capable of more reliable absolute fluorescence quantum yield measurements.

In order to measure the fluorescence quantum yield, the total number of emitted and reflected photons must be known. Because of the non-Lambertian nature of all physical samples, measurements in one geometry are insufficient. An integrating sphere can be used to measure the absolute fluorescence quantum yield [60–62]. However, integrating spheres are easily contaminated resulting in significantly reduced throughput and fluorescence in the UV-region [63–65] where many commonly used fluorophores have their excitation spectrum. Goniometric measurement devices do not have this problem.

The theory and mathematics for determining the absolute fluorescence quantum yield is presented in the appendix of publication IV. Without the need to make any assumptions of Lambertian behaviour of fluorescence emission, the fluorescence quantum yield can be calculated from goniometric measurements by

$$Q(\mu) = \frac{\int_0^{\pi/2} \left[ \sin(2\theta) \int \lambda \frac{i_s(\mu, \lambda, \theta)}{I_{std}(\mu, \theta)} \beta_{std}(\mu, \theta) d\lambda \right] d\theta}{\mu \int_0^{\pi/2} \sin(2\theta) \left[ 1 - \frac{I_s(\mu, \theta)}{I_{std}(\mu, \theta)} \beta_{std}(\mu, \theta) \right] d\theta}, \quad (3.4)$$

where  $\mu$  and  $\lambda$  are the excitation and emission wavelength, respectively, and  $\theta$  is the viewing angle. Parameters  $I_s$ ,  $I_{std}$  and  $i_s$  are the reflected signal from the sample, the reflected signal from a non-fluorescent reference and the fluorescence signal from the sample per unit wavelength interval, respectively, and  $\beta_{std}$  is the reflection radiance factor of the non-fluorescent reference standard. The factors  $i_s/I_{std} \cdot \beta_{std}$  and  $I_s/I_{std} \cdot \beta_{std}$  are the bispectral luminescent radiance factor and the reflection radiance factor of the sample, respectively. The equation assumes cylindrical symmetry from the reflectance and fluorescence emission and the  $\theta$ -integration is done over polar angles. The assumption of cylindrical symmetry has been confirmed by measuring bispectral luminescent radiance factors of a Spectralon sample [56] with azimuth angles  $0^\circ$  and  $90^\circ$  and comparing the results. The  $\lambda$ -integration is carried out over the whole emission spectrum.

### 3.3 Measurement uncertainty

The uncertainty budget for the measurement of the bispectral luminescent radiance factor is presented in table 3.1. The uncertainty depends on the measurement geometry and excitation and emission wavelengths. In table 3.1 the uncertainty is given for 0 : 45 geometry with excitation and emission wavelength close to the excitation and emission maximum.

**Table 3.1:** Uncertainty in the measurement of the bispectral luminescent radiance factor,  $\beta_{L\mu}(\lambda, \theta)$  (publication IV).

Source of uncertainty	Standard uncertainty	Rel. uncert. in $\beta_{L\mu}(\lambda, \theta)$ (%)
Repeatability	0.28 %	0.28
Random noise	0.5 %	0.71
Calib. repeatability	0.2 %	0.2
CCD uniformity	1.0 %	1.0
CCD linearity	0.1 %	0.1
Ref. det. responsivity	0.3 %	0.3
Illum. and viewing angles	0.2°	0.12
Radiance factor of reference	0.8 %	0.8
Ref. sample holder alignment	0.75 %	0.75
Stray light	0.4 %	0.57
Wavelength (excitation)	0.15 nm	0.1
Wavelength (emission)	0.17 nm	0.2
Slit scattering functions	0.2 %	0.2
EMS dispersion	2 %	1.7
Combined standard uncertainty		2.5

The first three uncertainty components in table 3.1 are of type A and the rest are of type B. The first component is calculated as the relative standard deviation of the mean of several independent measurements of the bispectral luminescent radiance factor,  $\beta_{L\mu}(\lambda, \theta)$ . The second component represents the random noise of the emission spectrometer (EMS) and it has been calculated as the relative standard deviation of the mean of several consecutive signal readings of the CCD. The third component in the table represents the repeatability of the emission system responsivity calibration and it has been derived similarly to the first uncertainty component.

The CCD uniformity means the response uniformity between different pixels in the CCD array when illuminated with the same irradiation. The uncertainty component has been derived from measurements of the CCD signal when the emission monochromator is scanned and the excitation monochromator is kept at a fixed wavelength setting. The CCD linearity is the linearity of the CCD response with respect to integration time and the value has been given by the manufacturer [66]. The uncertainty due to reference detector responsivity comes from the reference detector calibration [67]. The detector has been calibrated in a reference spectrometer setup [68].

The uncertainty of the illumination and viewing angles comprises the uncertainty of the precision and alignment of the fluorescence sample holder and the turntable that is used to rotate the light collector. The standard uncertainty of the radiance factor of the reference is given in 0 : 45 geometry and it comes from the reflectance scale of the gonireflectometer discussed in publication II. The component of the reference sample holder alignment represents additional uncertainty in the radiance factor of the reference due to the poor stability and accuracy of the reference sample holder. The component is evaluated by calculating the effect of increased uncertainty in aperture-to-sample distance and illumination and viewing angles when determining the uncertainty of the radiance factor.

Uncertainty due to stray light has been estimated from the CCD signal when the emission monochromator wavelength setting is above the excitation monochromator wavelength setting. The uncertainty of the wavelength scale of the excitation and emission monochromators has been estimated by calibrating them against mercury emission lines.

The uncertainty due to slit scattering functions represents the uncertainty caused by the broadening of the fluorescence spectrum. It has been estimated by measuring the width of the reflection peak of a non-fluorescent reference standard at the emission spectrometer (full width at half maximum) and the width of the fluorescence spectrum of a fluorescence sample. The measured fluorescence spectrum is a convolution of the true fluorescence spectrum and the slit scattering function of the excitation and emission monochromators obtained from the reflection measurement. An estimate for the true fluorescence spectrum and the associated relative uncertainty due to the broadening has been calculated by using a simple model that the fluorescence spectrum and the reflected signal are of Gaussian shape. The last component in table 3.1 represents the uncertainty in the emission spectrometer dispersion. It has been estimated by setting the emission monochromator at a fixed wavelength and calculating the positions of two different mercury lines on the CCD. Then this measured dispersion value has been compared to the value obtained from the manufacturer given parameters that define the theoretical dispersion of the emission spectrometer [66, 69].

The uncertainty of each component in the bispectral luminescent radiance factor,  $\beta_{L\mu}(\lambda, \theta)$ , has been evaluated according to reference [37].

## 4 Conclusions

In this thesis, goniometric calibration facilities for reflectance and fluorescence measurements have been designed and developed (publications II-IV). Also, the significance of light scattering from source optics in goniometric diffuse reflectance measurements has been studied (publication I) and the theory and mathematics for a new method for determining the absolute fluorescence quantum yield has been developed (appendix of publication IV).

Light scattering from source optics can have a significant effect in the goniometric diffuse reflectance and bidirectional radiance factor measurements leading to errors of the order of 1 % as shown in publication I. Also, this effect may be at least partly responsible for the differences reported between goniometric and integrating sphere-based diffuse reflectance measurements [28].

The gonireflectometer described in [10] and publication I has been characterized for measurements in the ultraviolet and near infrared spectral ranges. Also, an extensive bilateral comparison has been carried out between the gonireflectometers at the TKK [10] and the PTB [26]. The comparison was carried out in the wavelength range 250 nm – 1650 nm. Such extensive goniometric comparisons are quite rare even though they provide valuable information on the reliability of the absolute reflectance scales of National Metrology Institutes. The agreement of the reflectance scales at TKK and PTB was found to be satisfactory between 300 nm – 1400 nm. Below 300 nm isochromatic stray light, low signal-to-noise ratio, wavelength accuracy and possible fluorescence from samples cause additional uncertainty to the measurements. Above 1400 nm the discrepancies can be mainly explained by sample translucency. Overall, sample translucency was found to have a significant effect on the reflection measurements, particularly for opal glasses in the near infrared region (publication II).

A goniofluorometer capable of measuring bispectral luminescent radiance factors in various measurement geometries has been designed and tested (publication III). To my knowledge, no measurement results of such an instrument have been previously published.

The theory and mathematics of a new method for measuring absolute fluorescence quantum yield has been developed (appendix of publication IV). The new method is based on goniometric measurements. It does not have the problems related to integrating sphere wall contamination leading to reduced throughput and fluorescence in the UV range or the problem of re-reflection of emitted light from sphere walls and re-absorption to the sample causing additional fluorescence and distorting the emission spectrum.

One of the most significant results of the thesis is the discovery of the non-Lambertian nature of fluorescence emission from solid amorphous material and the fact that the angular pattern of emission is not very tightly linked to the angular pattern of reflection (publication IV). In the future, this result can not be neglected in the colorimetric measurements and the measurements of fluorescence quantum yield, but measurement geometries must be carefully considered when making measurements or calibrations for high-accuracy applications. In this thesis, fluorescence emission from one standard amorphous material, namely Spectralon, has been studied. It is likely that the angular pattern of fluorescence emission depends upon the material properties of the used fluorescence standard and the preparation process of the standard which also affect the goniometric reflection properties [70].

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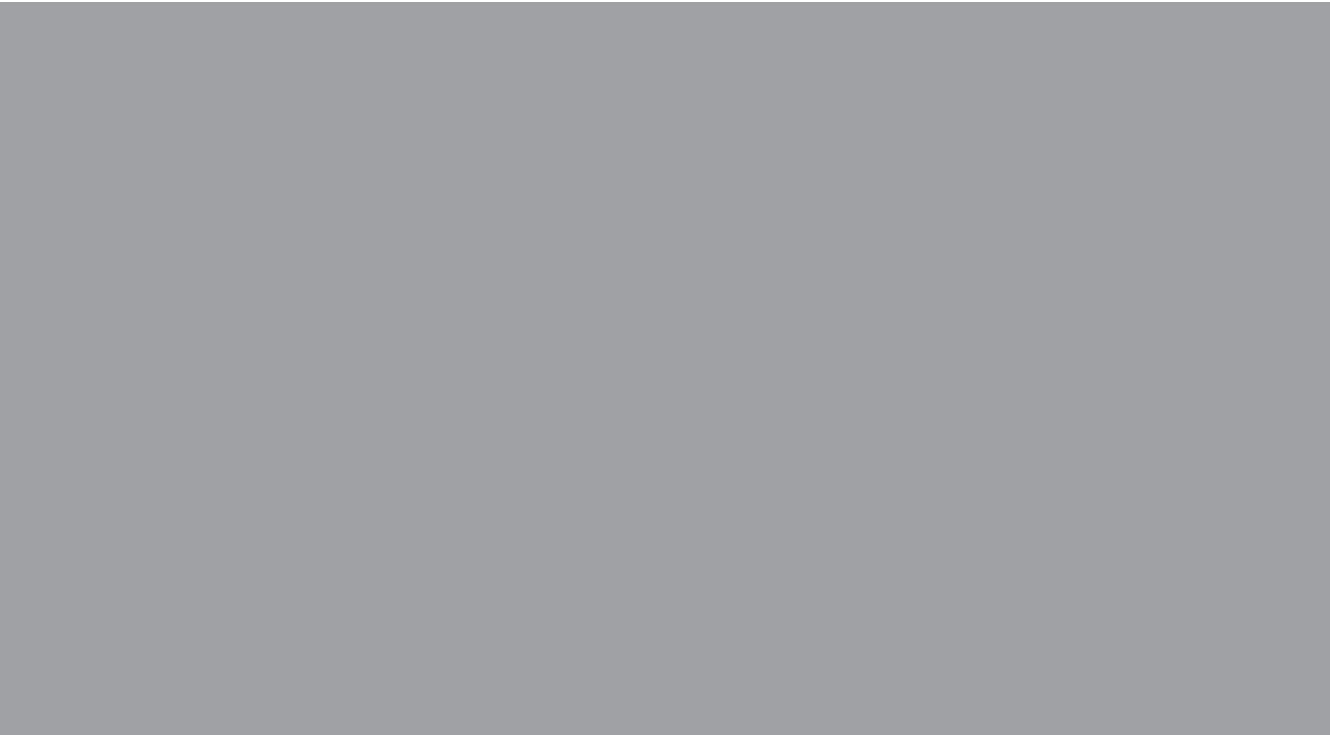
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