MEASUREMENT OF GONIOFLUORESCENCE IN PHOTOLUMINISCENT MATERIALS

Ferrero, A.[1], Bernad, B.[1], Velázquez, J.L.[1], Pons, A.[1], Hernanz, M.L.[1], Jaanson, P.[2], Martínez-Verdú, F.M.[3], Chorro, E.[3], Perales, E.[3] and Campos, J.[1]
[1] Instituto de Óptica, Agencia Estatal CSIC, Madrid, SPAIN, [2] Centre for metrology and accreditation, Espoo, FINLAND, [3] Dpto de Óptica, Farmacología y Anatomía, Facultad de Ciencias, Universidad de Alicante, Alicante, SPAIN
alejandro.ferrero@csic.es

Abstract

Fluorescent materials absorb light at a certain wavelength interval and then reemit it at other longer wavelengths, after about 10^{-8} seconds. Their colour appearance depends upon the combined effect of the fluorescent and reflected radiation. This work is focused in the measurement of the fluorescence of photolumiscent materials as a function of the irradiation and detection directions, which may be called as “goniofluorescence”. It was measured the spectral bidirectional luminiscence distribution function (BLDF) of five fluorescent samples at different combinations of irradiation and detection directions. The measurements were performed with the goniospectrophotometer GEFE, using monochromatic irradiation and a spectrorradiometer as detector. A general behaviour was observed for the five samples and the studied excitation wavelengths: the dependence of the excitation spectrum on the detection direction θ_s is almost symmetrical with respect to $\theta_s = 0^o$, decreasing towards high angles.

Keywords: Goniofluorescence, fluorescence, photoluminescence, spectrophotometry

1 Introduction

Fluorescence emission is a common luminous phenomenon occurring in many objects. These materials absorb light at a certain wavelength interval and then reemit it at other wavelengths longer than the incident one, after about 10^{-8} seconds and a little energy loss. Fluorescence occurs when an orbital electron of a molecule relaxes to its ground state by emitting a photon of light after being excited to a higher quantum state by some type of energy (Lakowicz 2007). Typically, the radiation emitted by fluorescence has a range of lower energy than the exciting radiation.

In last years, the measurement of appearance of objects has gained increasing relevance in industry. Particularly, it is demanded for reference standards and procedures for accurately characterizing the colour appearance of fluorescent materials, in order to predict it when they are irradiated under specified conditions of illumination. For a fluorescent material, the colour appearance depends upon the combined effect of the fluorescent and reflected radiation, so its spectrum will be the sum of two components: the reflected spectral component and the luminescent spectral component.

This work is focused in the measurement of the fluorescence of photolumiscent materials as a function of the irradiation and detection directions, which may be called as “goniofluorescence”. The relevant quantity to be measured was called Bidirectional Luminiscent Distribution Function (BLDF), which depends on the irradiation and detection directions and on the excitation and emission wavelengths. The measurements were performed with the goniospectrophotometer GEFE, a device designed and developed at IO-CSIC for goniospectrophotometric measurements (Rabal 2012, Bernad 2015).

2 Description of the goniospectrophotometer GEFE

The goniospectrophotometer GEFE (see Fig. 1), designed and developed at IO–CSIC, was conceived to measure the spectral Bidirectional Reflectance Distribution Function (BRDF) (Nicodemus 1977) at any pair of irradiation and detection directions, including out–of-plane

and actual retro–reflection geometries. It comprises three systems: the irradiation one, the sample-positioning one and the detection system. The first one is fixed, whereas the other two systems are mobile: The sample is placed with the required orientation relative to the incoming beam, while the detector is attached to a cogwheel so as to be able to revolve around the sample. This arrangement permits a fast and accurate sampling.

2.1 Irradiation system

The irradiation system is formed by a wide–band xenon lamp, which emits in the 185 nm - 2000 nm spectral range, and a Köhler optical system that allows uniformly and with a collimated beam the samples to be irradiated. In order to provide it with the capability of measuring fluorescence at different geometries, this system was upgraded with a monochromator in front of the xenon lamp, that allows spectral resolution at irradiation. It is a 300-mm focal length single monochromator in Czerny-Turner configuration (TMc300, Bentham Instruments Ltd), with two diffraction gratings, one of 1200 g/mm (250 nm - 1200 nm), and other of 830 g/mm (500 nm - 1800 nm).

2.2 Sample's positioning system

A six-axis robot-arm locates the sample quickly at the desired direction. The samples are held by the robot-arm by means of a vacuum sucker.

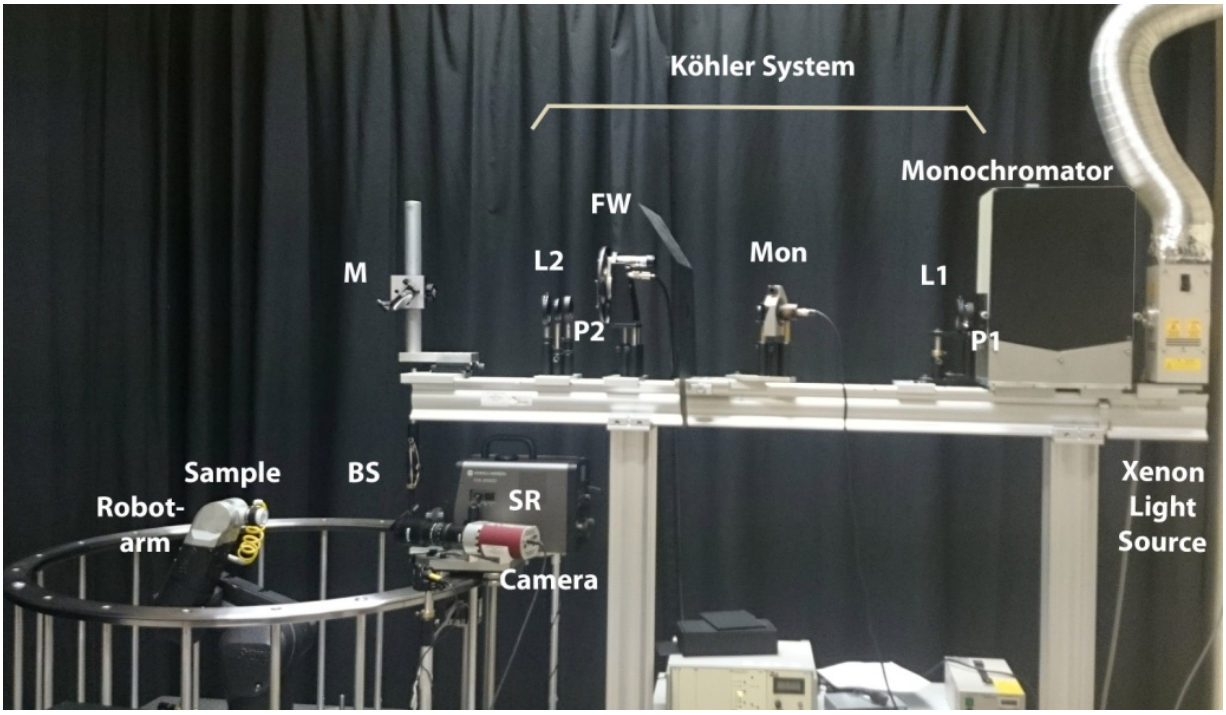

Figure 1 – Picture of the goniospectrophotometer GEFE. L1: first converging lens; P1: diaphragm 1; L2: second converging lens; P2: diaphragm 2; Mon: monitor; FW: filter wheel; M: fold mirror; BS: beamsplitter; and SR: spectrorradiometer.

2.3 Detection system

This system is formed by a spectroradiometer Konica-Minolta CS-2000 A, used to measure spectral radiance in the visible range (380 nm - 780 nm), with a variable field of view of 0.1°, 0.2° or 1°. It is mounted onto a platform that travels along a 1.03 m diameter cogwheel, whose center coincides with the location of the sample's reference system. The movement along the cogwheel is performed by means of a stepper motor with a step coder for position control.

3 Experimental conditions and samples

3.1 Samples

It was measured the spectral Bidirectional Scattering Distribution Function (BSDF) of five fluorescent samples at different combinations of irradiation and detection directions. These samples are "Spectralon® Fluorescence Standards" and, according to the product specifications, they provide highly stable, reproducible fluorescence reflectance over a long period of time in varying conditions, and the ideal matrix for inorganic fluors, which are photochemically stable, compared to their organic counterparts (Labsphere 2015).

3.2 Measurement conditions

The measurements were carried out using monochromatic irradiation and the spectrorradiometer as detector, which allows the spectral BSDF to be evaluated as a function of excitation wavelengths. The set of all spectral BSDF at different excitation wavelengths includes not only the spectral BRDF, but also a fluorescence distribution which could be called Bidirectional Luminescence Distribution Function (BLDF). We use the general term of BSDF (Bidirectional Scattering Distribution Function) to refer to both distributions.

The spectral BSDF was measured at the measurement geometries resultant from combining the irradiation and detection directions given by the following spherical coordinates (subscripts: i for irradiation and d for detection):

- Polar angle θ_i: 0º, 8º, 15º, 30º, 45º and 60º.
- Polar angle θ_d: from 0º to 80º (in steps of 5º).
- Azimuth angle ϕ_i = 0º.
- Azimuth angle ϕ_s = 0º and 180º.

Three excitation wavelengths were used for each sample, selected from a previous evaluation of their fluorescence at a single geometry (0º /45º).

The spectral FWHM was estimated in 7 nm for irradiation and in 3 nm for detection (between 380 nm and 780 nm). The measurement area is a 3 mm area at normal incidence, corresponding with a field of view of 1º. The system provides a 0.5º half angle of the irradiation solid angle and 2.5º half angle of detection solid angle.

A $0^o/45^o$ diffuse reflectance standard certificated by NPL (National Physical Laboratory) was used to determine the calibration factor of our system, and all spectral BSDF data were calibrated using that reference. The estimated total relative standard uncertainty was limited by the uncertainty of this reference (around 0.5 % with k=1).

4 Definitions

As previously mentioned, the BSDF can be expressed as the sum of the BRDF and the BLDF:

$$BSDF(\lambda_{em},\lambda_{ex}) = BRDF(\lambda_{ex})\delta(\lambda_{em}-\lambda_{ex}) + BLDF(\lambda_{em},\lambda_{ex}) \quad (1)$$

where λ_{em} and λ_{ex} are the emission and excitation wavelengths, respectively. We must notice that these distribution functions depend on both the irradiation and detection directions, although not explicitly stated.

By expressing Eq. 1 as:

$$BSDF(\lambda_{em},\lambda_{ex}) = BRDF(\lambda_{ex})\left[\delta(\lambda_{em}-\lambda_{ex}) + \frac{BLDF(\lambda_{em},\lambda_{ex})}{BRDF(\lambda_{ex})}\right] \quad (2)$$

we obtain the BSDF as the product of two factors. The first one (BRDF) contains the functional dependence on the irradiation and detection directions which is common for both reflected and fluorescent light. The second factor (BLDF/BRDF) is a function that expresses how differently the reflected and fluorescent light are scattered by the material. This second

factor can be expressed as the product between the emission spectrum (α) and the excitation spectrum (β):

$$BSDF(\lambda_{em}, \lambda_{ex}) = BRDF(\lambda_{ex})[\delta(\lambda_{em} - \lambda_{ex}) + \alpha(\lambda_{em})\beta(\lambda_{ex})] \quad (3)$$

where:

$$\alpha(\lambda_{em}) = \frac{BLDF(\lambda_{em},\lambda_{ex})}{max[BLDF(\lambda_{em},\lambda_{ex})]} \quad (4)$$

and

$$\beta(\lambda_{ex}) = \frac{max[BLDF(\lambda_{em},\lambda_{ex})]}{BRDF(\lambda_{ex})} \quad (5)$$

The emission spectrum is normalized by the maximum value within the emission wavelength range. We assume that the emission spectra are independent on the excitation wavelength, that is, the ratio in Eq. 4 is invariant with respect the excitation wavelength (Tominaga 2015).

5 Results

The Donaldson matrices (Billmeyer 1980, Donaldson 1954) at $0^o/45^o$ for the five studied samples are shown in Fig.2, in which the colour code is expressed in logarithmic scale [N = $\log_{10}$ (Radiance factor)]. According to the formalism given in Eqs. 1-5, the data in Fig. 2 can be expressed as in Fig. 3, where emission and excitation spectra are shown for every sample. Notice the especial case of the sample USFS-210-020, which presents a double fluorescent distribution. In this case, only the excitation spectrum corresponding to the emission at longer wavelengths is presented.

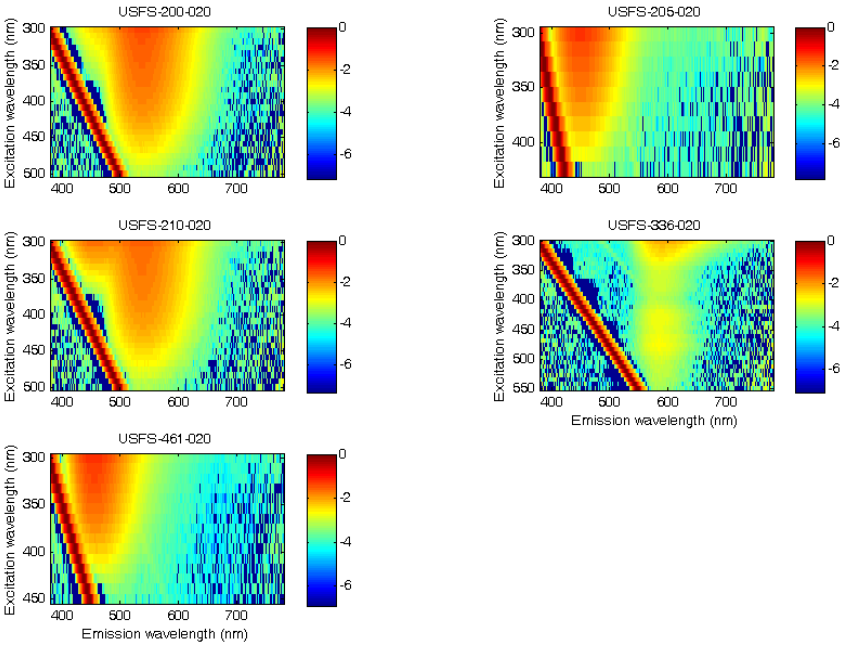

Figure 2 – Donaldson matrices at $0^o/45^o$ for the five studied samples.

We examined the dependence of the excitation spectra of these samples upon the irradiation and detection directions. Different excitation wavelengths were selected for every sample to have a good representation over the complete excitation wavelength range according to the results obtained and presented in Fig. 3.

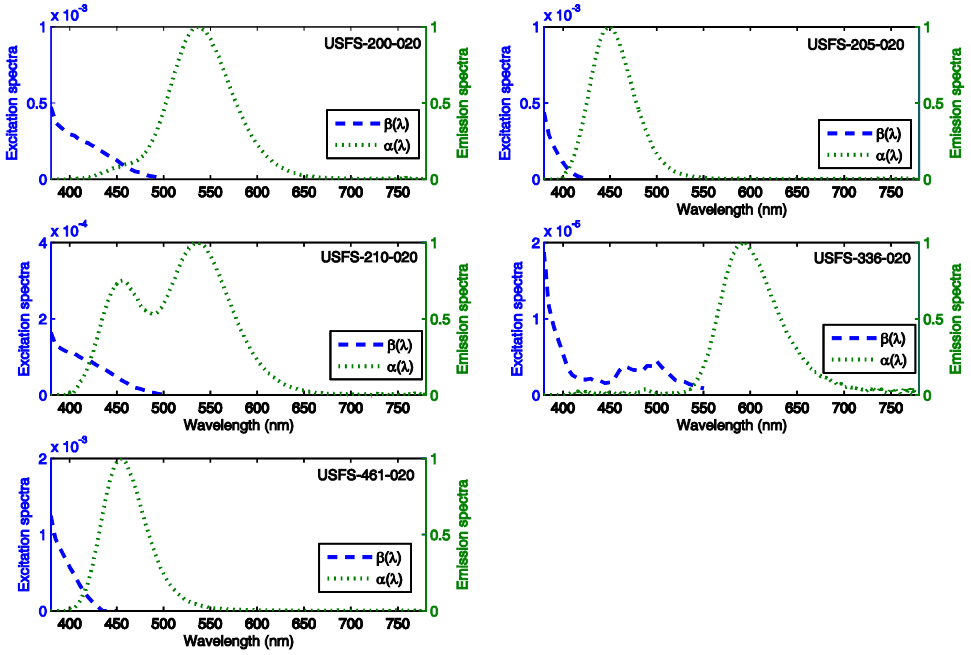

Figure 3 – Emission and excitation spectra at 0°/45° for the five studied samples.

The values of the excitation spectra of the samples are given for these three different excitation values in Figs. 4, 5 and 6 (short, intermediate and long excitation wavelengths, respectively). Every plot in the figures represents a different sample, which is identified by its name. Y-axis represents the value of the excitation spectrum, whereas X-axis represents the detection angle with respect to the normal of the sample (θ_s), allowing negative values of this variable for directions in the half incident plane containing the irradiation direction. The curves for four different irradiation angles (0º, 30º, 45º and 60º) are shown in every plot.

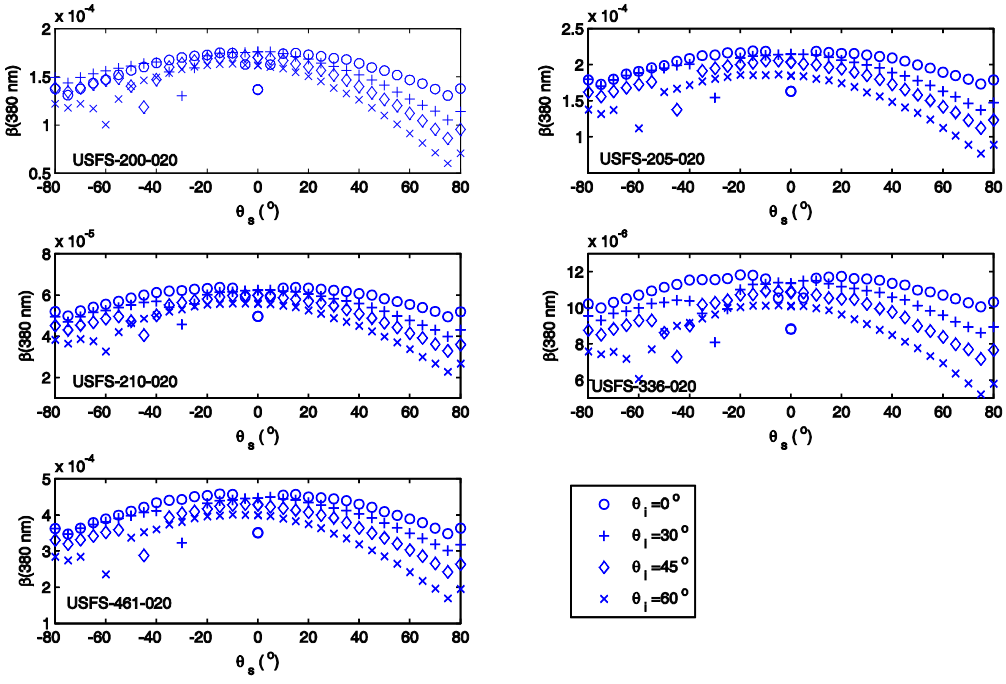

Figure 4 – Dependence on the irradiation and detection directions for the studied samples (short excitation wavelengths).

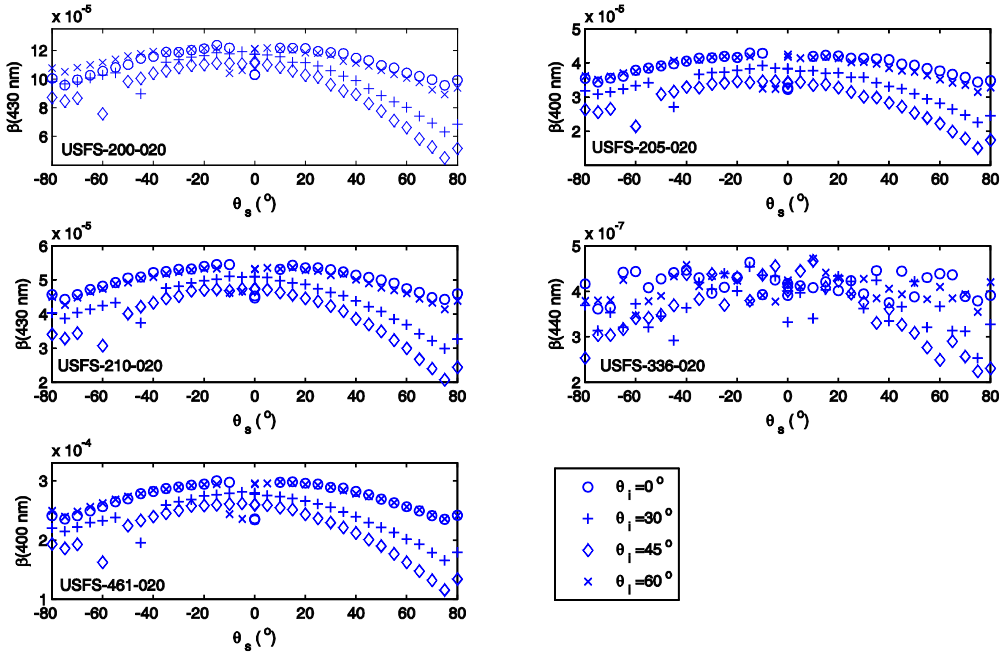

Figure 5 – Dependence on the irradiation and detection directions for the studied samples (intermediate excitation wavelengths).

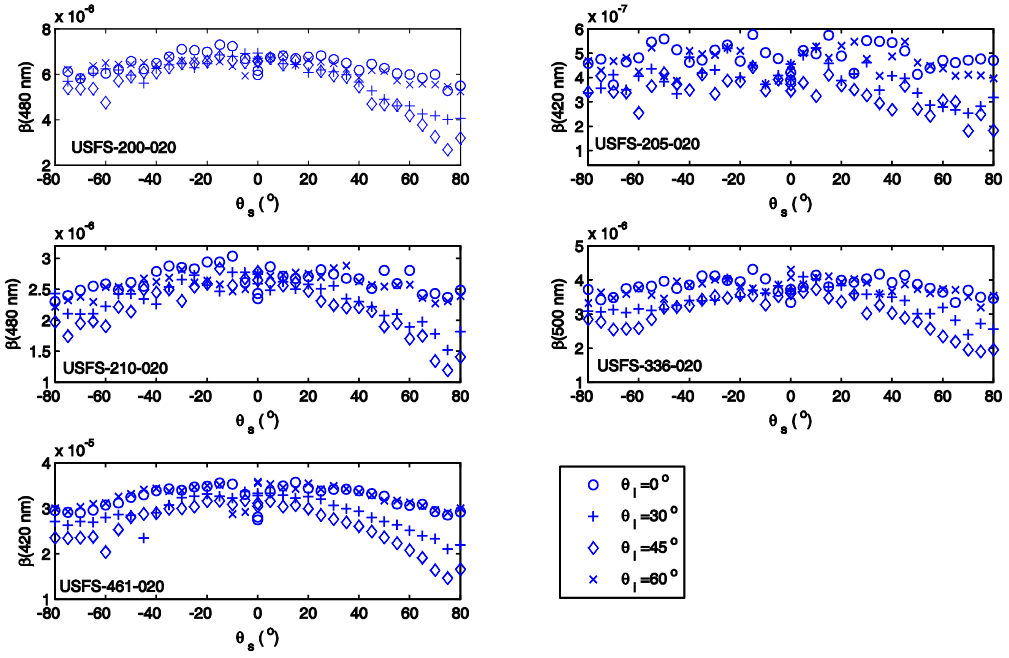

Figure 6 – Dependence on the irradiation and detection directions for the studied samples (long excitation wavelengths).

A general behaviour was observed for the five samples and the three different excitation wavelengths: the dependence of β upon the detection direction θ_s is almost symmetrical with respect to θ_s = 0°, decreasing towards high angles. The symmetry is lower for higher irradiation angles, for which β declines with a steeper slope for positive θ_s values (directions in the half incident plane containing the specular direction) than for negative ones. In addition,

it is observed that its values decreases when approaching to retroreflection directions (detection direction coincides with incidence direction).

Regarding the dependence upon the irradiation angle θ_i, it is observed that, in general, β declines with steeper slopes for higher irradiation angles. The only exception is found for the highest used θ_i (60º) at intermediate and long excitation angles, for which the dependence of β on θ_s is very similar to the one obtained for (θ_i = 0º) (see Figs. 4-6). This effect is more clearly shown in Fig. 7, where the value of β at θ_s = 60º [normalized to its value at θ_i = 0º and θ_s = 10º (instead of 0º to avoid the retroreflectance effect)] was plotted versus θ_i, for every sample (at different plots) and for every excitation wavelength (at different marker styles). In this figure, it can be observed that the dependence on the irradiation angle is similar for all sample, and that it is also very similar for a given excitation wavelength.

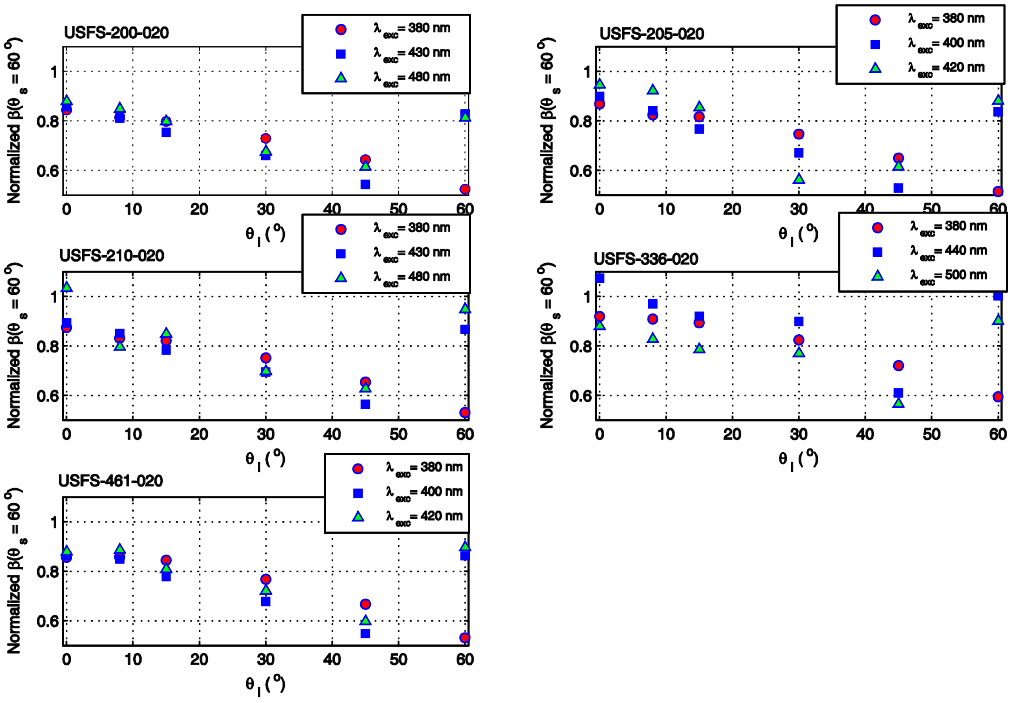

Figure 7 – Dependence of β on the irradiation angle θ_i. It was normalized to its value at θ_i = 0º and θ_s = 10º.

6 Discussion and conclusions

The variation of the excitation spectrum of fluorescence with the irradiation and detection directions (that we can name as “goniofluorescence”) is the relevant variable to specify the variation of colour of fluorescent materials. It was found that this variation was not appreciably different for the five studied Spectralon® fluorescence standards, which suggests that it is independent on the colour of the fluors in the material. It would mean that the characterization of the goniofluorescence and the spectral BRDF of just one of these standards would allow the colour of other standards to be calculated for any other irradiation and detection direction, as long the emission and excitation spectra at one pair of directions are known for the fluor added to the Spectralon®. We suggest that the excitation spectrum should be constant with the measurement geometry in the case of a Perfect Reflecting Diffuser (PRD) (any photon is scattered by the material at a random direction regardless incidence angle or wavelength) because the fluorescence event can be considered also perfectly diffuse. In the real world, as in the case of the Spectralon®, the diffusion mechanism depends on the incidence angle or on the wavelength, and in the different way for reflected photons than for photons produced by fluorescence, whose emission direction should be independent on the incidence angle. This may explain why the factor β is not constant with measurement geometry. We must remember (Eq. 5) that it is calculated as the quotient between the maximum value of the BLDF and the BRDF value at the excitation wavelength. We know from previous studies that the BRDF of

Spectralon® presents a higher reflectance toward high irradiation and detection (positive) angles (Ferrero 2012), and also peaks around the retroreflection directions (Rabal 2014). The mechanisms involved in those effects do not affect fluorescent light and, since the BRDF of Spectralon® is dividing when β is calculated, it would explain the steeper slopes for high irradiation and detection (positive) angles and the retroreflection effect observed in Figs. 4-7. In those figures, only the features independent on the irradiation angle can be due to the particular diffuse propagation of this fluorescent light, as it is the case of symmetric dependence of β on θ_s with respect to $\theta_s = 0^o$.

Finally, we must noticed that an important advantage of the formalism proposed to analyze the goniofluorescence (defined as the variation of the excitation spectrum of fluorescence with the irradiation and detection directions) is that the result is independent on calibration factors, since it is based on relative values of the BSDF at the wavelength of maximum fluorescent emission and at the excitation wavelength, at the same irradiation and detection direction.

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