# Fluorescence in Some Colour Standard Tiles

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## Abstract

Fluorescence has been detected in some white standard tiles intended for the calibration of spectrophotometers for colour measurements. These standards could introduce errors in measurement if they are used to calibrate instruments with a type of illumination different to that used in the determination of spectral reflectance. This work anlyse instrument's characteristics that influence this subject, and present some results on how colour coordinates of different samples change when they are measured against one of this standards.

## Introduction

How we see coloured objects is a well studied phenomenon. The perceived colour of an object is determined by the spectral composition of the light leaving it, the spectral reflectance for the case of non-transparent materials. The spectral reflectance is usually determined using a spectrophotometer, and the colour computed for specific illuminants. Independently of the type of spectrophotometer used, the measurement is made by comparing wavelength by wavelength the light reflected by a sample to that reflected by a reflectance standard, usually a white ceramic tile. In order to correctly calculate the sample reflectance at a given wavelength, the detector signal should correspond to the fraction of light reflected by the sample illuminated by that wavelength. This is always the situation for non-fluorescent materials.

The Spectrophotometry Laboratory at the Instituto de Física Aplicada is the National Laboratory in Spain for this kind of measurement. In the course of our work, we have detected the presence of fluorescence in some white ceramic tiles intended for the calibration of spectrophotometers for colour measurements. These standards could introduce errors in measurement if they are used to calibrate instruments with an illumination type different to that used in the spectral reflectance determin-ation. The error quantity in colour coordinates for this reason will depend on the spectral distribution of the sample to be measured, and on some characteristics of the measurement instrument, besides the illumination type.

The spectral reflectance of a white ceramic tile that presents fluorescence, has been measured in our laboratory with two different instruments. The different results obtained and how colour coordinates of different colour sample change when they are measured against this standard, are presented in this work. Bandwidth is also an input variable for this study and results are given as a function of it.

## Theoretical Background

Fluorescence is a phenomenon that occurs when a substance absorbs radiation of a certain wavelength, or range of wavelengths, and re-emits photons of different wavelength.

In a non-fluorescent molecule, photons are absorbed but they immediately drop back to the original energy state, dissipating energy in the form of heat or simply emitting a photon of equal wavelength. If there are molecules in the pigment mixture that fluoresce, the resulting spectrum is a combination of a number of factors: a) the reflectance of the non-fluorescent material; b) the absorbance of the fluorescent material due to the excitation of electrons to a higher energy state; c) the emission spectrum of the fluorescing material. Truly a mess to interpret since both the absorption and fluorescence depend on the distribution of wavelengths in the illuminant used.

Spectrophotometers come in two types. First, there are those that scan over the spectrum. Almost always from higher wavelengths to lower using monochromatic illumination of the sample, stepping from wavelength to wavelengtrh with a detector that indiscriminately collects the reflected or emitted photons. This type of instrument is typical of most analytical UV-VIS spectrophotometers.

The second type measures in opposite way. The source illuminates the sample with all wavelengths at once, then the spectral analysis is performed after the light is reflected by the sample, usually by use of an array of silicon photodiodes. This is a diode array spectrometer. For materials that do not fluoresce, the spectral data obtained from either of these instruments will, in theory, be identical. If a fluorescent material is part of the pigment mix, the results are greatly different.

For this type of samples, spectral reflectance measurement and colour computed from them can not be properly determined with the first type of spectrophotometers described. If the second type is used, the source has to match a CIE standard illuminant, If this is not accomplished, surface colour of fluorescent samples has to be measured by the double monochromator method.

## Experimental Measurements

The spectral reflectance of a white ceramic tile, that is used for the calibration of some industrial colorimeters, has been measured in our laboratory using two different spectrophotometers. A Perkin Elmer Lambda 9 UV-VIS-NIR spectrophotometer (spectral illimination type) and a Jhonnie Reilholfer diode array spectrophotometer (wide spectrum illumination type, matching D65 standard illuminant). Both instruments have got a 1 nm bandwidth. The results obtained can be seen at figure 1. Notice that the curve corresponding to the mesurement in the scanning spectrophotometer shwos up a combination of absorbance and emission, since the detector is unable to differentiate between photons of different wavelengths.

The second curve, that one corresponding to the measurement in the diode array spectrophotometer shows a typical fluorescent peak that appears as an enhancement to the reflectance.

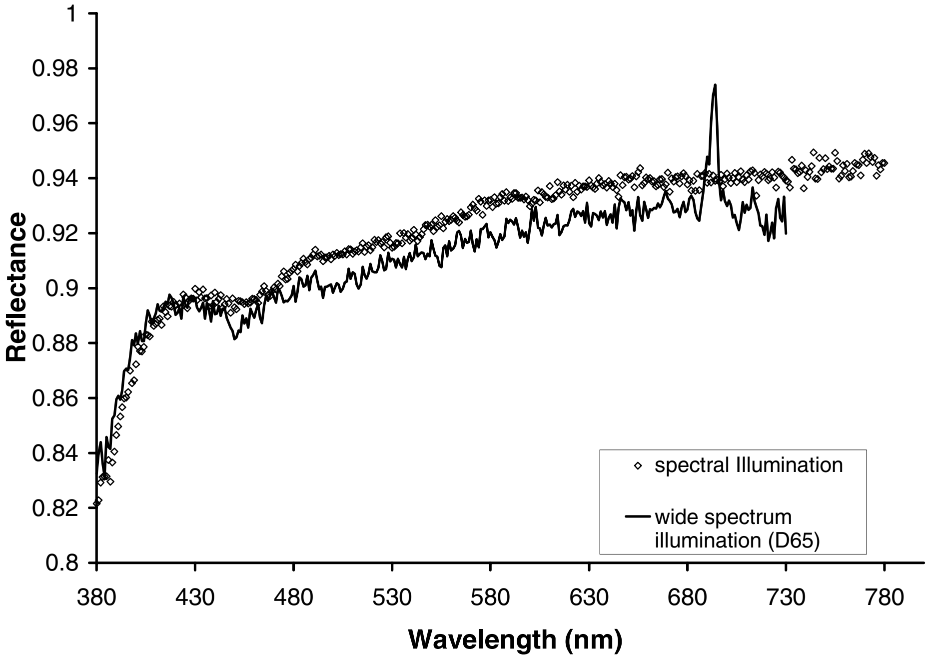


*Figure 1. Spectral reflectance of a fluorescent white ceramic tile.*

From both reflectance values we have calculated tristimulus values as well as chromatic parameters in the uniform space CIE 1976 (L*a*b*). Colour difference obtained, ΔE, calculated with the formula recommended by the CIE in CIELAB system are represented in Figure 2. CIE 10º and CIE 2º Observers and Standard Illuminants A and D65 were used in the calculations. Colour differences larger than 0.5 CIELAB units are obtained in all cases.

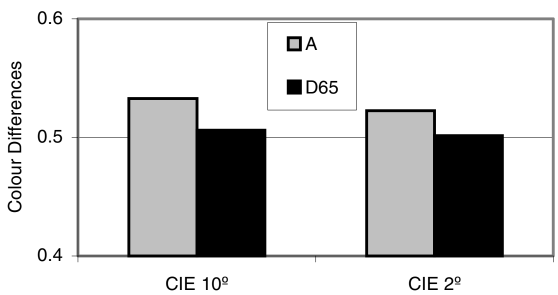


*Figure 2. Colour differences between reflectances measured in both spectrophotometers*

It is very usual that this type of samples, unknowing the presence of fluorescent pigments inside them, will be calibrated (by measurement of the spectral reflectance) using scanning spectrophotometers. The obtained values are then used to calibrate industrial colorimeters. In agreement with the results shwon in this work, errors in the measurements will then be introduced.

## Effect on Colour Coordinates of Different Samples

In order to study the effect that a white standard that present fñuorescence, produces on the colour coordinates of samples measured against one of them, we have calculated the tristimulus values and the chromatic coordinates of five non-fluorescent samples identified with the names: Deep Blue, Green, Mid Grey, Red and Orange. To determine the spectral reflectance of each sample, both spectral reflectance curves of the white tile, measured in the two spectrophotometers have been used.

Colour differences ΔE obtained, are represented at figures 3 and 4 for CIE 10º and CIE 2º observers respectively.

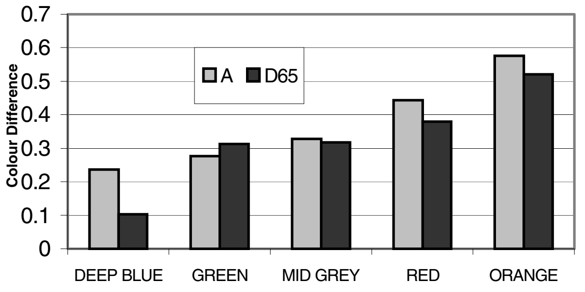


*Figure 3. Colour differences obtained for each sample for CIE 10º Standard Observer*

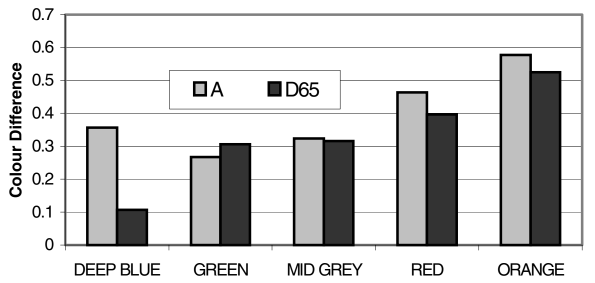


*Figure 4. Colour differences obtained for each sample for CIE 2º Standard Observer*

As it can be seen the effect is small for the deep blue and green samples, since they have small reflectance where the fluorescence is present. The colour differences are noticeable for red and orange samples, as it could be expected from its spectral reflectance curves. Special attention should be paid in mid grey sample. Althougth the colour difference is about 0.3 CIELAB units, it could be important if it is used to calibrate linearity scale of spectrophotometers. In general colour differences are more important for illuminant A than D65.

## Spectral Bandwidth Error

Spectral bandwidth error, defined as the difference between a spectral distribution and its effective value within a given bandwidth, is always present in spectral measurement since any detection system needs a minimum bandwidth to produce a reasonable signal to noise ratio. The amount of this error depends on the bandwidth range and the distribution's shape.

In colour calculation, the bandwidth has got a further effect because the summation step must be a divider of the spectral bandwidth according to CIE.

Besides spectral bandwidth, slit function of a spectrophotometer influences the calculation of tristimulus values. This slit function, according to the optical properties of the monochromator, could be symmetrical or asymmetrical. In practice, good quality instruments have got a symmetrical slit function, but there are other that have not.

Effective spectral distribution values for 5, 10 and 20 nm bandwidth were calculated as:

$$R_{ab} = \frac{\int_{ab} R(\lambda)B(\lambda)d\lambda}{\int_{ab} B(\lambda)d\lambda}$$

where $R(\lambda)$ is the original spectral reflectance, $B(\lambda)$ is the slit function that has been assumed to be triangular in this job; and ab, the measurement spectral interval. The measured spectra have been interpolated to obtain values every 0,1 nm in order to minimise integration errors in the previous equation. The interpolation has been made through splines functions. Effective spectral distribution values for 5, 10 and 20 nm are shown in figure 5.

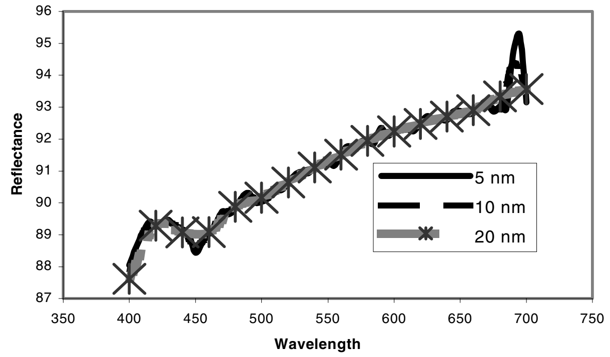


*Figure 5. Effective spectral distribution values for 5, 10, and 20 nm bandwidth.*

To estimate the error attributable to bandwidth, colour coordinates were calculated for the white ceramic tile, as measured in the diode array spectrophotometer, at bandwidth of 5 nm, 10 nm and 20 nm and then the colour difference between these coordinates and the corresponding to the 1 nm spectra was calculated. Colour coordinates were calculated with a summation step equals to the bandwidth, and between 400 and 700 nm in all cases.

Total colour differences for Illuminats A and D65 and Standard Observer CIE 10º due to bandpass error are plotted in figure 6. Notice that this is not the real difference because of the truncation (400 to 700 nm) used.

Only at 20 nm bandwidth the colour differences are important because the fluorescence peak disappears as it can be seen at figure 5.

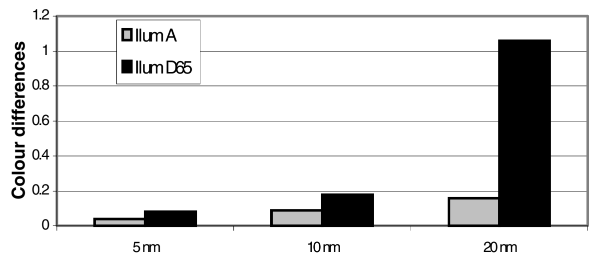


*Figure 6. Colour differences obtained in a white ceramic tile for effect of the bandwidth used*

## Conclusions

An analysis on the presence of fluorescence in some white ceramic tiles used as standards has been made in this work. The results obtained show that the effect of the fluorescence is not negligible. If they are used as standards for measurements of colour coordinates of blue or green samples, the effect is small, but it is important in red, orange and yellow hues. For achromatic samples, the effect is also noticeable since the colour differences are comparable or higher than the equivalent to the uncertainty of the measurement (typical values of 0.16 CIELAB units are obtained).

The effect of fluorescence could be observed for bandwidths values as large as 10 nm.

## References

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