

Fluorescence Spectroscopy

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Measurement of Optical Brightening Agents in Samples Using the FL 6500 Fluorescence Spectrometer and Solid Sample Holder

light, as fluorescence, in the blue-violet region of the visible spectrum (420 – 470 nm). The result is an increase in the perceived whiteness, by increasing the amount of blue light reflected and masking the natural yellow color. Excessive use of OBAs has been found to cause papers to have a clear bluish tint. Additionally, most brighteners will naturally fade over time when exposed to oxygen and UV light.^{1,2}

This application brief demonstrates the use of the PerkinElmer FL 6500 Fluorescence Spectrometer with Solid Sample Holder for the rapid qualitative analysis of OBAs in materials, with minimal preparation required.

Introduction

Optical brightening agents (OBAs), also known as fluorescent brightening agents (FBAs) or fluorescent whitening agents (FWAs), are dyes commonly used to increase the apparent whiteness and brightness of paper, textiles and detergents. These compounds absorb light in the UV-visible region (usually 340 - 370 nm) of the electromagnetic spectrum and re-emit the

Optical Brightening Agents

As well as being present in paper and textiles from manufacturing, OBAs are commonly found in whitening laundry detergents, providing the function of replacing the brightening agents which have been lost from the textile during previous washes.³ As a result, chemicals classified as optical brightening agents are commonly found in domestic waste waters which also contain detergent.⁴

The first compounds to show promise for use as optical brighteners were the stilbenes (Figure 1), which had originally been developed for use in paper but were found to be relatively versatile. There are now many derivatives based on stilbene, each with certain characteristics depending on their preferred application. Approximately 80% of all OBAs produced today are stilbene derivatives, for example, Figure 2.⁴

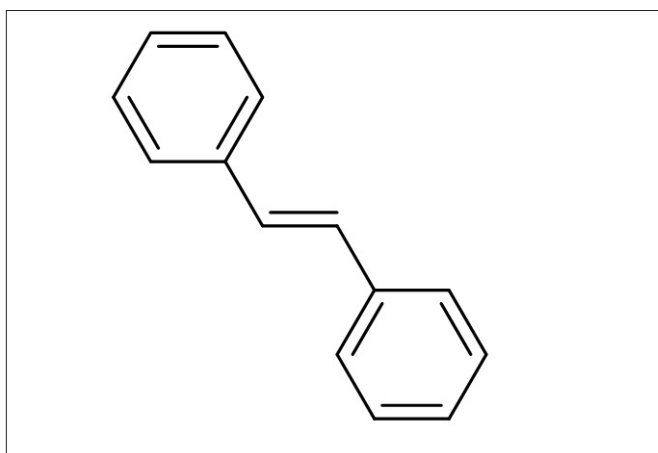


Figure 1. Chemical structure of trans stilbene.

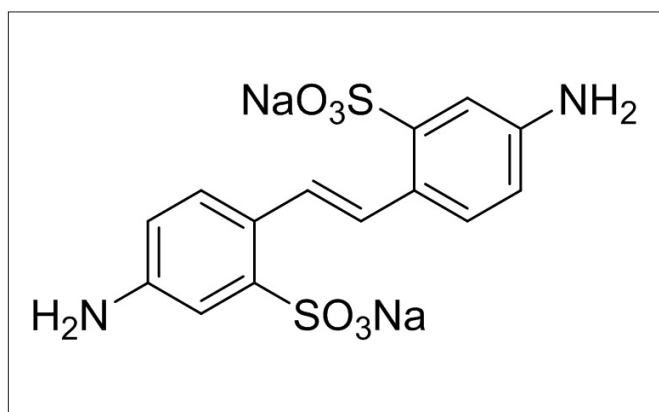


Figure 2. Chemical structure of 4,4'-Diamino-2,2'-stilbenedisulfonic acid.

An important chemical aspect of stilbene and its derivatives is that the ethylene group is in the *trans*- conformation. The *cis*- configuration exhibits steric hindrance between side groups on the non-adjacent benzene rings, consequently making the molecule non-planar. This non-planarity would somewhat reduce the conjugation and thus shift the absorption region into the UV region, preventing fluorescence. Furthermore,

trans- stilbene gains rigidity when it is attached to fibers, increasing the intensity of fluorescence by a factor of 4-5, relative to the stilbene in solution. However, a disadvantage of stilbene-based OBAs is that they do not bind well to man-made fibers such as nylon, relying solely on adsorption. In this case, pyrazoline based brighteners (Figure 3) are far more useful.⁵ Other OBAs are based on derivatives of coumarin, naphthalene dicarboxylic acid, and heterocyclic dicarboxylic acid, for example.⁴

Fluorescence and Phosphorescence

OBAs increase the apparent whiteness of paper and textiles by increasing the fluorescence of the paper. Fluorescence is a radiative process in which the radiation emitted has a longer wavelength and thus lower energy than that of the absorbed radiation. This process occurs following excitation (absorption of light) and vibrational relaxation to the ground vibrational state of the excited electronic state. Fluorescence emission then occurs, with a timescale of 10^{-9} – 10^{-7} s, by transition from the excited electronic state to the ground electronic state. The longer wavelength light emitted means that materials containing OBAs will commonly appear with a blueish hue under light with a UV component. Fluorescence is frequently confused with phosphorescence, the phenomenon responsible for materials which 'glow in the dark'. However, unlike fluorescence, molecules which exhibit phosphorescence undergo intersystem crossing following vibrational relaxation. This mechanism occurs by transition from a singlet to a triplet state, followed by return to the ground singlet state with emission of light. This quantum mechanically forbidden transition is what causes phosphorescence to take place over seconds, hours or even days.^{6,7}

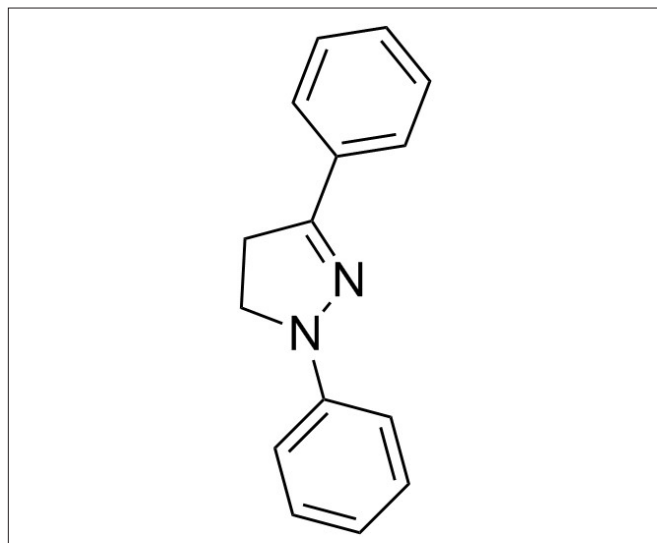


Figure 3. Chemical structure of 1,3-Diphenyl-2-pyrazoline.

Experimental

A small section (20 x 20 mm) of several 'white' materials (business card, printer paper, filter paper, and window blind material) were cut and clamped in place in the Solid Sample Holder accessory of the PerkinElmer FL 6500 Fluorescence Spectrometer (Figures 4 and 5). The instrument scanning conditions are shown in Table 1.



Figure 4. PerkinElmer FL 6500 fluorimeter.

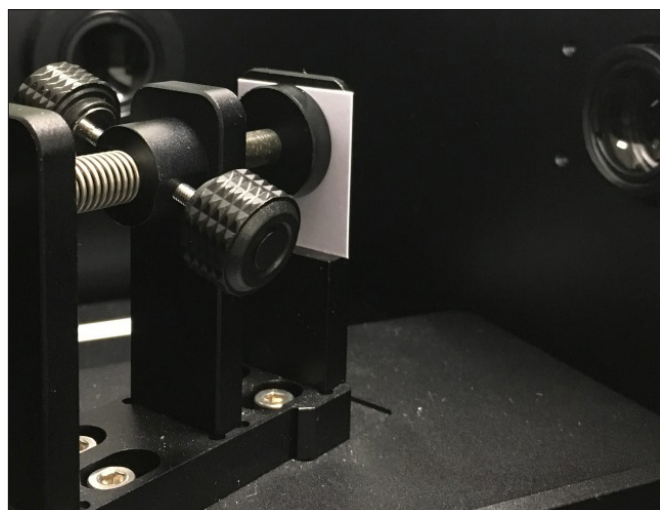


Figure 5. Solid Sample Holder for the FL 6500 and FL8500 series fluorescence spectrometers, with a clamped business card sample.

Table 1. Operating parameters using for the FL 6500 Fluorimeter.

Instrument Settings		
Source	Flash power (kW)	120
	Frequency (Hz)	100
	Excitation filter	Air
	Initial dark correction	On
Excitation	Wavelength (nm)	359
	Slit width (nm)	5
	Correction	On
Emission	Wavelength scan (nm)	375 - 500
	Slit width (nm)	10
	Correction	On
	Filter	Air
Acquisition	Scan speed (nm/min)	240
	Response width (nm)	5
	PMT voltage (V)	400 (low)
	PMT gain	x1

Results

Emission spectra of the various materials are shown below in Figure 6. A peak maximum around 440 nm, corresponding to the presence of OBAs, was observed in the printer paper, business card and window blind samples. However, the filter paper sample demonstrated no peak maximum over this wavenumber range.

Conclusion

This application brief demonstrates the use of the PerkinElmer FL 6500 Fluorescence Spectrometer with Solid Sample Holder for the rapid qualitative analysis of OBAs in materials, with minimal preparation required. Samples are simply cut to size, to fit in the Solid Sample Holder, and scanned. Additionally, when paired with Spectrum FL software, with its intuitive features and workflow based method editor, analysis can be carried out quickly and easily.

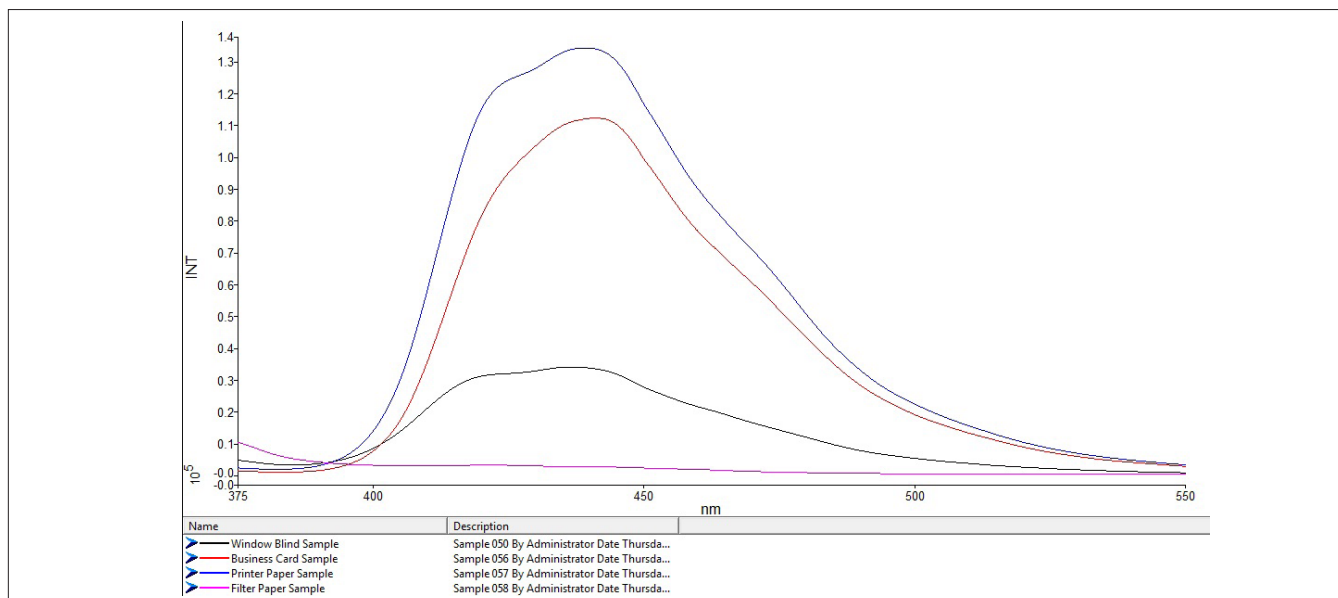


Figure 6. Emission spectra of various 'white' materials including printer paper (blue), business card (red), window blind (black), and filter paper (pink).

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