Optical properties of paper at 337.1nm

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Here, we are reporting on the 337.1 nm radiation scattering and fluorescence spectra for white and colored bond paper (100 μm thick) using an N_2 laser of 1 μJ pulse energy (t_{FWHM} = 3.8 ns). Fluorescence lifetimes in the order of 10 ns and transit-times in the order of 1 ns were obtained. No fluorescence changes were caused by the short term paper irradiation.

Keywords: Laser; fluorescence; paper.

En este trabajo se reporta sobre la dispersión de radiación de 337.1 nm y los espectros de fluorescencia de papel bond blanco y de color (100 μm de espesor) usando un láser de N_2 que emite pulsos de 1 μJ de energía (t_{FWHM} = 3.8 ns). Se midieron tiempos de vida de fluorescencia en el orden de 10 ns y tiempos de transito alrededor de 1 ns. No se manifestaron cambios en la fluorescencia como consecuencia de la radiación aplicada.

Descriptores: Láser; fluorescencia; papel.

PACS: 87.64; 32.50.+d

1. Introduction

White bond paper is commonly used to detect UV laser radiation. In particular, reflected and transmitted violet-blue fluorescence can be observed when 337.1 nm wavelength radiations are falling on it. When light strikes a sheet of paper, some of it is reflected back in a directed reflection. The remainder penetrates into the sheet, where it is scattered in all directions. One part will eventually be reflected back or transmitted forward from the sheet as diffuse radiation, another part is absorbed inside the paper, producing fluorescence, and the remainder is transmitted through the sheet [1]. The paper's micro-topographical surface structure, the free surface area, and the size, shape, and chemical composition of pigments and fibers are known to influence these optical properties [2].

Optical properties of paper are normally studied with continuous wave visible light (400-500 nm). Reflectance, brightness, Y-value and opacity require the elimination of UV-radiation in order to avoid the influence of paper fluorescence [3-5]. However, if the presence of a fluorescent agent in the paper needs to be determined, then a UV light source is necessary [6-8]. Such fluorescent agents are used as whitening agents in white paper [6,8] or as dyes in colored paper [9]. Here we present a study of the optical properties of commercial bond paper when it is radiated with 1μJ pulsed light, 250 W peak, with 3.8 ns FWHM and 337.1 nm wavelength produced by a N_2-laser. The elapsed time of this pulse make it possible to measure the fluorescence lifetime and the transit-time of the light through the sheet. Although it is reported [10] that absorption photons with energies greater than $\sim$3.6 eV (λ <340 nm) can lead to direct photolysis, or can induce photo oxidative degradation of paper, the pulse energy used in our experiments produces no fluorescence changes in the short term. Traditionally [11,12] UV in museums should not exceed continuous 20 mW/m^2 irradiances in order to limit damage done to the paper. In our experiments, average UV powers in the order of 4×10^3 mW/m^2 during laser irradiation (in the order of tenths of ns), which takes place at frequencies of tenths of pulses per second, were used. So, under these conditions we have measured the reflected and transmitted scattering at 337.1 nm, as we did with the fluorescence spectra and fluorescence lifetimes on the reverse side of different colored papers. The delay time in the paper of the scattered 337.1 nm wavelength radiation is also measured.

2. Angular dependence of the laser light scattering

Figure 1 shows the goniometric arrangement to measure the light scattering on paper at 337.1 nm. A home made Blumlein N_2 laser, 1 μJ, 250 W peak, at 337.1 nm ($\Delta\lambda_{FWHM}$ = 2.6 nm, Δt_{FWHM} = 3.8 ns) air operated at 70 mbar is enough in all our experiments. A microscope slide and a Motorola MRD500 photodiode were used to monitor the laser light and to trigger the detection system. The measured reflectance of the slide is 17%. A rectangular (1.7 mm $\times$ 0.9 mm) spot at the sample is obtained with a 2.54 cm diameter BK7 glass lens (15 cm focal length).

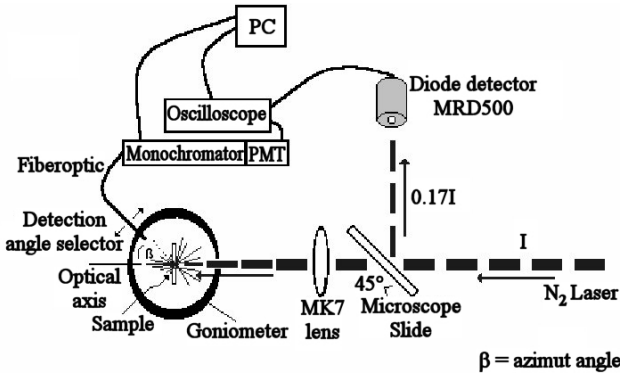

FIGURE 1. Laser scattering explorer.

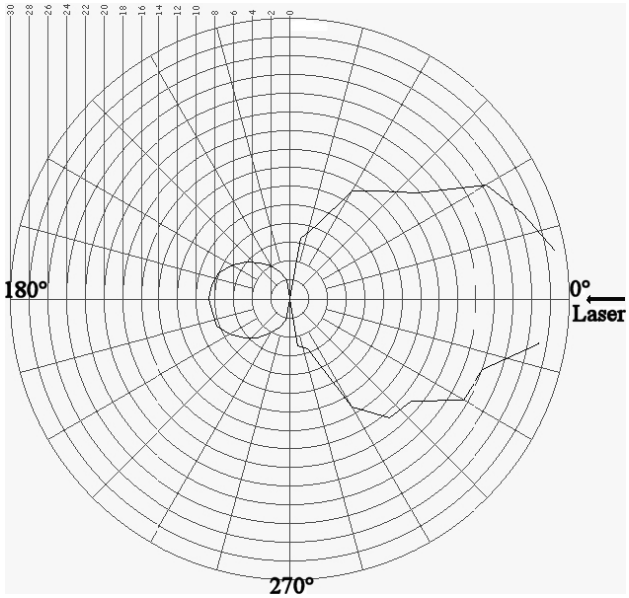

FIGURE 2. Normalized laser scattering vs the azimuth angle ß in white bond paper, measured at 6.3cm from the probe.

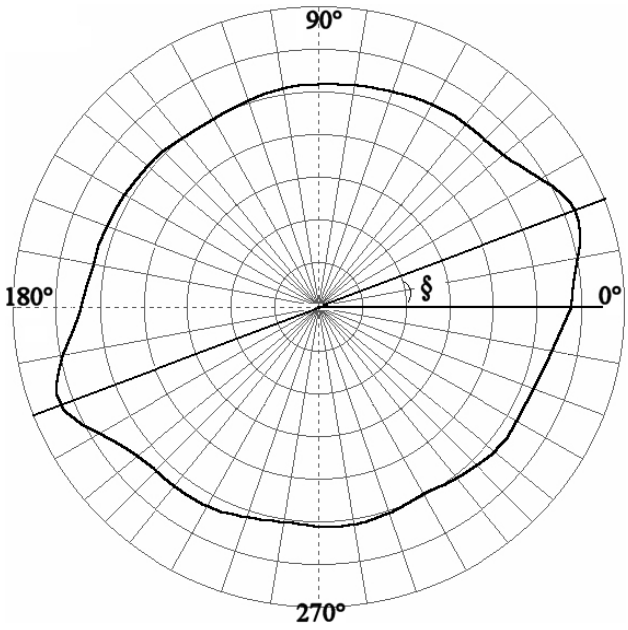

FIGURE 3. Normalized laser scattering around the optical axis at ß = 40° in white bond paper.

The scattered light is collected by an Edmund Scientific E38956 quartz fiber optic light guide (6.2 mm core diameter, 91.4 cm length). The optic light guide is manually positioned at different angles with respect to the forward on-axis direction of the laser beam in increments of 5°. The fiber optic is always located at a radial distance of 6.3 cm. The scattered light is analyzed in a 0.27 m Digital Scanning Monocromator (Spectra Pro 275 from Acton Research Co.) and measured by a Hamamatsu R955 PMT. The laser reference and scattered pulses are registered by a 2440 digital Tektronix oscilloscope. A PC is used to control the operation of the monochromat and to save the signals measured by the oscilloscope, after an average of 30 pulses every 5°degrees. Figure 2 shows the relative peak power of laser light scattered versus the azimuth angle ß by white paper (COPAMEX Facia Bond, 75 g/m^2, 94% whiteness, 100μm thick). Because of the physical construction it was not possible to measure around 180°. Figure 3 shows the relative peak power by the goniometric rotation around the optical axis at ß= 40°. The elongated form of the pattern and the angle §in Fig. 3 results from the dominant fiber direction in the paper, which depends on the paper production[2].

Similar relative intensity of the scattering distributions is obtained from colored paper. Table I shows the relative peak power at 337.1 nm scattered at 0° from different colored papers.

3. Transit-time of the light in the paper

Figure 4 shows the arrangement for measuring the time the 337.1 nm transmitted light was delayed by the perpendicular position of the paper in the path of the laser radiation. Both detectors are Motorola MRD500 photodiodes and the length cables and the position of the photodiodes were adjusted to give superposed signals when there was no paper in the laser path. A Melles Griot interference filter, 8 nm bandwidth (90%), centered at 339.2 nm was used to avoid paper fluorescence in the channel 2 detector. Figure 5 shows the reference signal and the delayed one from white paper. The scattered signal is delayed by 1 ns, which corresponds to a light speed of 10^5 m/s in the paper. Table I shows the time delay (dt) for the different papers used in our research.

TABLE I. Relative transmitted peak power at 337.1nm and delayed time caused by different colored papers, ß = 0°.

PAPER	*RELATIVE TRANSMITTED INTENSITY (a.u.)*	*DELAYED TIME Δt (ns)*
Green	***0.09***	***1.2***
Purple	***0.21***	***1.08***
Yellow	***0.58***	***0.98***
White	***0.60***	***1.08***
Pink	***1.00***	***1.06***

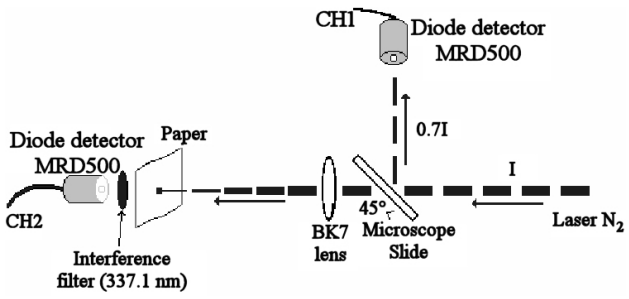

FIGURE 4. Arrangement to measure the transit time of 337.1nm radiation in paper.

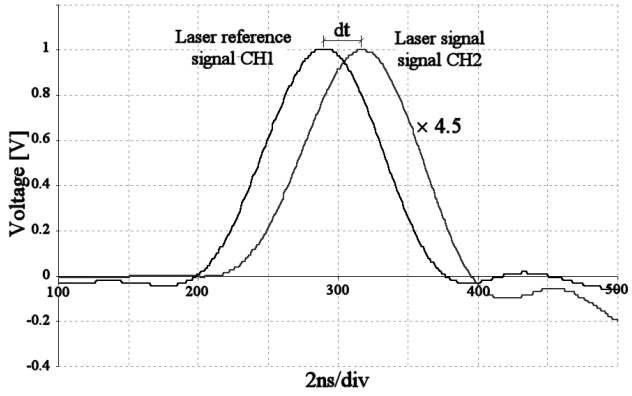

FIGURE 5. Time resolved laser reference pulse and delayed 337.1nm radiation in white bond paper.

4. Fluorescence of different colored papers

When the laser radiation is concentrated on the input of the fiber optic light guide, one can see the fluorescence of the guide. So, in order to avoid the fluorescence of the light guide, the fluorescence measurements were obtained from the reverse side of the paper, where the scattered light is weaker. The arrangement of Fig. 6 was used, where the probe was irradiated at 45° and the fluorescence was measured perpendicular to the reverse side of the paper. In order to achieve a large signal, two BK7 ball lens (10 mm diameter, E 32-748, from Edmund Industrial Optics) forming a fiber coupler, were used. Figure 7 shows the measured spectral fluorescence and scattered laser light of the white paper. The scattered 337.1 nm laser radiation is weaker than the fluorescence, and no fluorescence on the fiber input appeared. The fluorescence spectrum resembles the spectrum of the Blue-White Luminescent pigment SFS-461 used as a standard in the paper industry [13]. SFS-461 pigment, and commonly used fluorescence whitening agents in white paper, only work when ultraviolet light is present. Figure 7 shows too the fluorescence spectra of different colored papers under similar conditions. The fluorescence of green and purple papers is weaker than yellow, white and pink ones. Only the yellow and pink papers show two wavelength fluorescence intervals: the yellow one, from 350 to 420 nm and from 550 to 680 nm; the pink one, from 380 to 500 nm and from 570 to 700 nm (a mixture of white-blue and red colors). The fluorescence of purple and green papers shows spectra concentrated in the corresponding wavelengths of the electromagnetic spectra. Figure 8 shows the time evolution of the laser pulse and of the fluorescence of white paper at 500 nm. Table II shows fluorescence lifetimes at maximum wavelength fluorescence in the different emission intervals from the different papers (The fluorescence lifetimes were calculated accordinging to the time difference between the time of the peak fluorescence and the time when this falls to 0.33 of that peak). The fluorescence lifetimes at the two peak emissions, for yellow and pink papers, are different. It could be due to the two different colorants used in their production, but unfortunately we do not have any information about those components. Because of aging, paper loses its optical properties as time passes [13]. Measurements such as these presented here could be useful for studying the papers' long-term stability and how aging affects it [14].

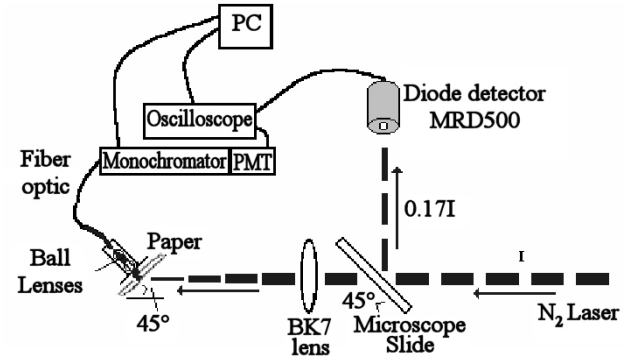

FIGURE 6. Arrangement to measure paper fluorescence.

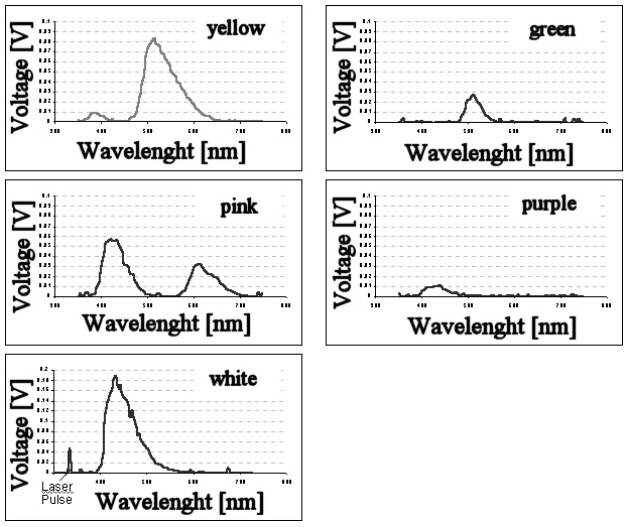

FIGURE 7. Paper fluorescence spectra by 337.1 nm excitation.

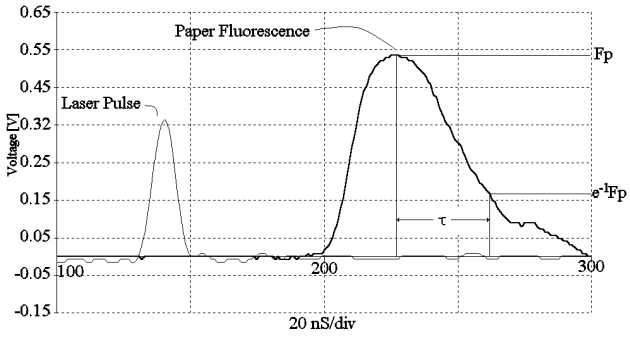

FIGURE 8. Time resolved laser reference pulse and fluorescence pulse of white paper.

TABLE II. Fluorescence lifetimes, τ, at λ_{peak} emissions, from different colored papers

PAPER	λ_{peak} *(nm)*	τ*(ns)*
Green	***505***	***9***
Purple	***435***	***8***
Yellow	***380 515***	***6 10***
White	***440***	***12***
Pink	***425 605***	***10 16***

5. Conclusions

Paper scattering, fluorescence spectra and transit and fluorescence lifetimes have been studied using a 337.1 nm N_2-laser. The backscattered light is almost four times larger than the forward one, so, in order to reduce the fluorescence from the optical components of the detection system, the reverse side of the paper was used to make fluorescence measurements. The goniometer makes it possible to determine the fluorescence patterns and the dominant fiber direction in the paper. Fluorescence spectra and life times of colorants in the paper can be measured with this system.

So, in order to find the presence and concentration of different colorants or components in the paper, it is only necessary to know the spectra and fluorescence lifetimes.

Scattering patterns and transit times of the laser radiation, which up until now have not been taken into consideration, could be useful to feed to models for simulating light scattering in paper [16].

1. D. Nyström, "Paper Optics", http://www.itn./iu.se/∼/iyan/Courses/Paper-Optics/Paper-optics-dn.pdf (16/04/2004).
2. The Paperloop Group, "Paper Help Contents", http://www.pponline.com/toolkit/paperhelp/2-1.shtml (16/04/2004).
3. N. Pauler, "Paper Optics", Mo Do Paper, Markaryd (1993).
4. Finnish Paper Engineer's Association and TAPPI, Paper Physics, Vol. 16, Papermaking Science & Technology Series, Chapter 4, (1998).
5. W.W. Wendlandt and H.G. Hecht,"Reflectance Spectroscopy" Interscience Publishers, (1966) p. 154.
6. T1212 sp-98 Standard practice-1998, "Light Sources for evaluating papers including those containing fluorescent whitening agents" TAPPI-1998.
7. M. Archard and A.J. Michell, "Diffuse Reflectance Ultraviolet Spectroscopic Studies of Paper" Varian Instruments at work UV-49, (December 1989).ansysinc.com/products/spectr/uv/atworks/uv49.pdf (16/04/2004).
8. M. Dubreuil, "Introduction to Fluorescence in Fiber Recycling" Paper Recycling Challenge-Deinking & Bleaching (1997) p. 212.
9. E. Koretsky, "The Coloring of Pulp in Alkaline Papermaking". Abbey Publications, Inc. 2004. http://palimpsest.stanford.edu/byorg/abbey/ap/ap01-4/ap01-411.html (16/04/2004).
10. W. Kantek, S. Pontzien, D. Muller- Hess, K. Troschke, and R. Teule "Probing the limits of paper and parchment laser cleaning by multi-spectral imaging" http://www.artinnovation.nl/ventura/engine.php?Cmd=getpicture&P_site=3168P_self=203 (25/04/2004).
11. B.C. Patkus, "Protection from light damage", Northeas Document Conservation Center File://A:tleaf24.htm (26/04/2004).
12. Littlemore Scientific Engineering, "UV Light Monitor Type 763" http://www.elsec.couk/763.htm (26/04/2004).
13. http:/www.labsphere.com/uploadDocs/FTS%20Fluorescence%20Standards_239.pdf (16/02/2004).
14. The National Academy of Sciences, "Preservation of Historical Records (1986)", Chapter 4 "Paper" http://www.nap.edu/openbook/030903681X/html/33.html (16/04/2004).
15. Bruce Arnold "ASTM's Paper Aging Research Program". http://palimpsest.stanford.edu/byanth/arnold/astm-aging-research/ (14/04/2004).
16. P. Edström, M. H. Granberg, M. Gulliksson, "Some Ideas on Models and Methods for Light Scattering in Paper", Mid Sweden University, Report number: R-01-10, January 2001, http://www.mh.se/fscn (16/04/2004).