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Original article

Monitoring the natural aging degradation of paper by fluorescence

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ABSTRACT

This study deals on the natural degradation of paper monitored by using laser induced fluorescence. Samples of aged paper dated from 1730 to 2009 were analyzed in the spectral region from 540 to 750 nm. A structural evolution of the paper has been detected through variations of the fluorescence spectra characteristics. Results indicate that changes ascribed to the paper fibers as cellulose, hemicellulose and lignin, can be monitored in function of their natural aging time. Therefore, fluorescence spectroscopy is an appropriate technique to investigate the degree of paper deterioration. Furthermore, the emission spectrum allows to estimate their manufacture date.

1. Research aims

This work is focus on the use of laser fluorescence as a non-destructive technique to evaluate the degree of aging in paper. This technique allowed to evaluate the degree of aging paper in both, ancient as well as in contemporary papers. When the paper begins its degradation process, it is observed a wavelength shift in the emission spectra of the bands, also is detected variations in their intensity whit the aging of the paper. Then, this non-destructive technique may be implemented in order to monitoring the conservation state of cultural heritage items and classify the samples according to their manufactured date and aging state.

2. Introduction

Materials based in organic compounds may decompose through a wide range of degradation mechanisms, among which the interaction with environmental factors, such as acid hydrolysis, oxidative agents, light, air pollution or the presence of microorganisms stand out. [1]. In the case of the paper, deterioration is an inevitable process which provides and interesting research area, however neglected and its study is at most underdeveloped [2,3]. Also, it is important to remark that the preservation of documentary heritage is one of the biggest challenges facing paper conservators today [4].

The extensive use of paper in documents, both recent and ancients, demands monitoring the deterioration process, including aspects such as aging, loss of permanence, and durability [5]. Those aspects are intimately influenced by intrinsic factors as chemical composition, and the regulation of the structural state, which influences other physical properties such as the optical behavior of the paper.

Deterioration of different kind of paper has been studied through non-destructive techniques, for example ATR-IR spectroscopy [6–10], ultrasonic techniques [11,12], IR and Raman spectroscopy [13–20] and atomic force microscopy [21]. All of these techniques are able to identify degradation effects on paper exposed to accelerated ageing treatment. In addition, most of the studies about the paper deterioration have analyzed pure cellulose and/or pulps in accelerated ageing conditions [22], and less attention has been given to the accelerated ageing in real paper [23]. Then, there is almost no available literature on paper deterioration under real conditions, due their degradation occurs with a slow rate, for which the monitoring is required to be performed during many years. Also, ancient paper was made using long cellulose fibers with the addition of sizing compounds, while contemporary

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paper, say the used for laser-print such as the analyzed in this work, is manufactured from cellulose fibers as principal component, but also has hemicellulose and lignin as secondary components [9,24]. This makes too complicated the analysis of contemporary paper naturally aged. However, these biopolymeric chains deteriorate differently, which permits the degradation analysis of the chains and therefore of the paper aging. In this work were analyzed paper manufactured between 1730 and 2009. The chemical behavior of the paper was sensed by using the standard laser fluorescence method and the optical properties were interpreted in terms of its structural evolution and then, they were related to the production date of the paper. A novel non-destructive technique based on laser induced fluorescence was implemented in order to monitoring the conservation state of cultural heritage items and classify the samples according to their manufactured date.

3. Experimental

The analyzed samples consist of paper dating from 1730, 1750, 1805, 1829, 1894, 1989, 1990, 1992, 1994, 1996, 1997, 1998, 2001, 2002, 2003, 2004, 2005, 2006, 2007, and 2009, these dates were estimated from the manuscripts contents. These samples were selected randomly from different sources in order to analyze the aging under real conditions. Papers were directly measured by fluorescence spectroscopy in order to obtain its optical behavior. The emission spectra were obtained by irradiating the paper with an excitation source, in this case using a Omnicrome argon ion laser of maximum power of 3 W and tube current of 10 mv/A, with line at 488 nm. In addition, it was used a fiber optic with a probe at 45° of incidence angle and a colored glass filter at 550 nm, in order to guide the collected fluorescence light to a high-resolution spectrometer Ocean Optics, Inc. model SF2000.

The fluorescence spectroscopy method proposed in this work for the paper aging analysis is based in previous results using organic compounds as extracts of leaves and the used wood for maturation of alcoholic beverages, which give optical information about the denaturation of compounds such as the chlorophyll, protein complex, and wood extracts, in the spectral region between 540 to 750 nm [25–31]. The proposed method is capable of analyzing the natural degradation of the paper according with its organic components. This configuration allows to get the fluorescence contribution of the organic compounds and therefore, the behavior of the samples aged by time under real conditions can be obtained. The fluorescence experiment generates information on the molecular behavior of the compounds which can be associated with the photosynthetic process, such as in chlorophyll species, and in our case in the cellulose, which is formed as the result of glucose photosynthesis, and represents the main content of wood. The same experimental configuration was maintained for all the samples in order to compare the fluorescence intensity between paper samples. Then, a deconvolution process was applied to the obtained spectra in order to distinguish the different contributions which are associated with the paper aging processes.

4. Results and discussion

The classical spectrum of steady-state fluorescence emission for the wood shows two maximums in 488 nm and 580 nm, the bandwidth is extended from 378 nm to 750 nm, and the width at half-maximum (FWMH) rates of 115 nm. Therefore, the fluorescence emission spectrum can be decomposed in two Gaussian curves (sub-bands) centered at each one of their maximums, according with that, one sub-band has its center in 488 nm whilst the other one is centered in 580 nm, this last is a minor curve [25].

The second sub-band obtained from the fluorescence experiment contains information about the molecular behavior for the

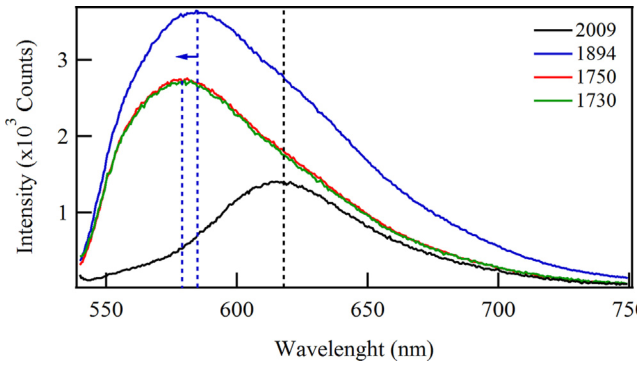

Fig. 1. Emission spectra of ancient paper compared with a contemporary paper.

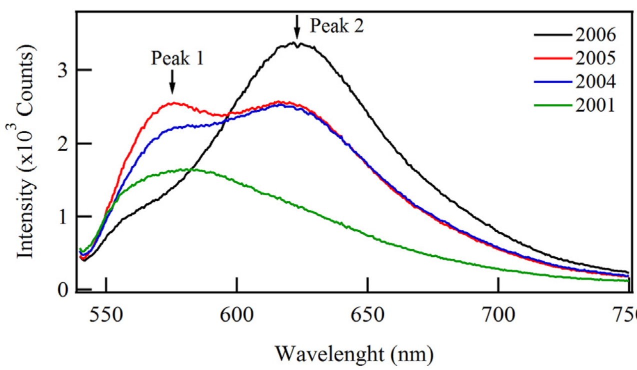

Fig. 2. Emission spectra of contemporary paper manufactured under same conditions.

compounds which can be associated with the photosynthetic process [32]. This sub-band was selected to analyze the fluorescence effects of the paper when samples where excited with an argon ion laser using a wavelength of 488 nm. In a previous work, it was found that this sub-band provides information on the structural changes in organic samples. In particular, the fluorescence intensity can be related with the concentration of components extracted from the wood and is a suitable technique to analyze the maturation time in alcoholic beverages [25].

The age effects on the paper are observed in Fig. 1, ancient paper samples (1894, 1750 and 1730) have a fluorescent band with high intensity. In the case of the 1894 paper, the band is centered in 586 nm and when paper gets old, this band has a blue shift to a lower wavelength. For the paper dated 1750 and 1730, having a difference of only 20 years between them, both centered in 575 nm. The shape of ancient paper spectrum is very similar to the emission obtained from wood, which indicates that ancient paper contains large chains of cellulose.

Contemporary paper has a band centered on 618 nm, and the first band founded in the three ancient samples is practically inexistent in the contemporary paper. Then, the observed changes of the emission spectra when paper is aged are associated with changes occurred in its structure indicating denaturalization of the paper.

Fig. 2 shows the fluorescence spectra of contemporary paper, which present notoriety structural changes in few years. The spectra were measured in 2009, the dates (2006, 2005, 2004 and 2001) labeled in each curve were estimated on basis of the paper content, even though this procedure is a crude approach to estimate the paper date, the selected samples correspond to the same type (laser-print paper) but manufactured at different time. Contemporary paper present two peaks located at about 575 nm (peak 1) and 623 nm (peak 2).

From the fluorescence spectrum of the paper dated 2006, is observed that the first peak is centered at 555 nm, but its intensity