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3D Fluorescence Mapping: A promising Technique for the Analysis of the Degradation of Pigments

Stefania Porcu[1], Michela Podda[2], Giovanni Brodu[2], Stefano Columbu[2], Daniele Chiriu[1]

[1] *Department of Physics, University of Cagliari, SP8, 09042 Monserrato (CA), Italy*
[2]*Department of Chemistry and Hearth Science, University of Cagliari, SP8, 09042 Monserrato (CA), Italy*
stefania.porcu@dsf.unica.it, m.podda70@studenti.unica.it, giovanni.brodu@unica.it, columbus@unica.it, daniele.chiriu@dsf.unica.it

***Abstract* – This study promotes 3D Fluorescence Mapping as an effective, non-invasive technique for analyzing pigments. By exciting pigments with different wavelengths, the method highlights characteristic fluorescence emissions that reveal chemical composition and detect degradation processes such as oxidation, fading, and molecular rearrangement. Despite conventional techniques like XRD and FTIR, which often require physical sampling, 3D Fluorescence Mapping allows real-time, surface-level analysis with no damage to the object.**

I. INTRODUCTION

Cultural heritage objects are often composed of fragile materials. The study of these materials, particularly pigments and organic dyes, is crucial for understanding their composition, provenance, and long-term stability under environmental stress. However, traditional analytical techniques such as X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, and gas chromatography-mass spectrometry (GC-MS), while highly informative, often require sampling or direct contact with the object's surface[1][2][3][4].

In response to these challenges, in recent years there has been a significant shift toward the development of non-destructive analytical methodologies and among these, fluorescence-based techniques have shown considerable importance [5][6]. Fluorescence spectroscopy allows the study of the characteristic emission of certain compounds when excited by specific wavelengths, facilitating the identification of chromophores and fluorophores commonly found in both inorganic pigments and organic dyes. However, conventional fluorescence spectroscopy is limited by its unidimensional nature, often capturing data only at fixed excitation or emission wavelengths.

To overcome these limitations, 3D Fluorescence Mapping is a multidimensional analysis able to obtain comprehensive fluorescence responses across a range of excitation/emission wavelengths allowing the detection of subtle molecular changes [7].

While 3D Fluorescence Mapping has been successfully applied in fields such as environmental monitoring, biomedical diagnostics, and food science, its application in the analysis of cultural heritage materials remains underexplored [8].

This study aims to evaluate the sensitivity, accuracy, and diagnostic potential of 3D Fluorescence Mapping on a set of historically significant pigments and organic dyes, suggesting that 3D Fluorescence Mapping could be a good method to regularly check the condition of objects and help prevent damage over time. [4][8].

II. MATERIALS AND METHODS

A. Pigments

The pigments were purchased from Kremer company and analyzed without any purification.

B. Methods

The three-dimensional fluorescence mapping of pigments was performed using a spectrofluorometer, a Jasco FP-8050, with a 450 W Xenon lamp as the excitation source. The maps were collected with an excitation range of 360–600/700 nm and an emission range of 400–850 nm with a 5 nm spectral bandwidth for excitation and emission.

III. DISCUSSION

A. 3D Fluorescence Mapping

Three-dimensional fluorescence mapping offers a non-invasive path that overcomes the dimensional limitations of conventional fluorescence spectroscopy.

Collecting data over a full range of excitation and emission wavelengths produces a spectral 3D map exclusively representative of a sample's molecular

composition and environmental conditions.

Cultural materials often contain mixtures of organic and inorganic compounds, aging products and additives, all of which may fluoresce differently depending on their microenvironment. 3D fluorescence mapping is highly sensitive to such variations and is non-contact and capable of scanning large surface areas, making it ideal for routine monitoring of heritage objects.

Additionally, changes in fluorescence intensity, emission peak shifts, and band shape distortions serve as early indicators of chemical alterations such as oxidation, hydrolysis, or molecular rearrangement.

The technique can be also applied together with Principal Component Analysis (PCA) and/or Component Prediction Method (PARAFAC), enabling pattern recognition, pigment classification, and statistical tracking of degradation progress over time.[9]

B. Pigments degradation

The colors in artworks and artifacts can fade or change over time, mostly because of exposure to light, air (especially oxygen), and moisture.

Organic pigments, which come from natural sources like plants, insects, or minerals (for example, madder, cochineal, or indigo), are sensitive to light.[10] Their molecules absorb ultraviolet (UV) and visible light easily.

When this happens, the pigment gains energy that can then be passed on to oxygen in the air, creating reactive oxygen species (ROS).[11]

These are very reactive forms of oxygen that can damage the pigment's structure. Over time, this causes the pigment to lose its color or even disappear.

For example, the red pigment carminic acid (from cochineal) can lose its carboxyl group and change its structure, leading to fading. Indigo, a blue dye, can turn into other chemical forms that are less stable and change its color.[12]

These changes can happen faster depending on the local environment, things like pH, metal ions, or what kind of material the pigment is mixed with.

Inorganic pigments, which are often made from minerals or metals (like lead white, cinnabar, or azurite), are usually more stable than organic ones. However, they can still be damaged, especially if the binder they are mixed into begins to break down.[13]

For example, linseed oil, a common binder in oil paintings, can react with light and oxygen to form acids and other byproducts.[7] These byproducts can change the local environment around the pigment, making it more acidic and promoting harmful chemical reactions.

Some pigments may also react to air pollution or moisture. Cinnabar, for instance, can turn black when exposed to light and humidity due to a chemical change to metallic mercury.[14]

Humidity plays a big role as well. In humid conditions, water helps ions move around, which speeds up chemical reactions.

This is especially true in artworks made with materials that absorb water easily, like egg tempera or gum arabic. These changes can affect the pigment's crystal structure or even cause it to dissolve slowly.

Because these chemical changes can be very subtle, they are not always easy to see with regular tools. That's why 3D Fluorescence Mapping can help to detect even small changes in the pigment and binder by showing how their fluorescent signals change over time. This allows conservation experts to monitor artwork without damaging it, and to better understand whether the pigment itself is degrading or if it's being affected by changes in its environment.

IV. PRELIMINARY RESULTS

The results, confirmed by XRD analysis (Fig.1), refer to pigment 53:1, commonly known as Lake Red ($C_{34}H_{24}BaCl_2N_4O_8S_2$).

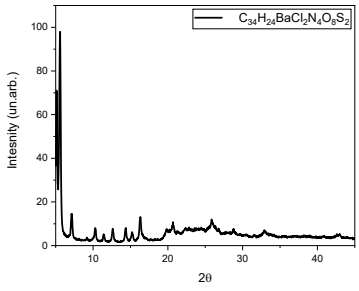
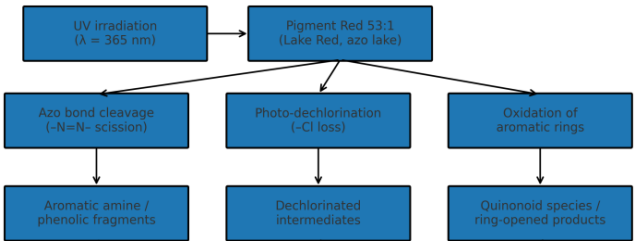


Fig. 1. X-Ray diffraction pattern of red lake pigment.

Pigment Red 53:1is an azo lake pigment with limited photostability under ultraviolet irradiation.

The principal degradation pathway involves cleavage of the azo bond (–N=N–), resulting in fading, loss of saturation, and a progressive color shift towards yellow-brown tones.

Additional processes such as photodechlorination and oxidative attack on the aromatic substituents further contribute to the instability of the pigment under UV exposure (Scheme 1).[15]



Scheme 1. Possible degradation pathways of red lake pigment.

To investigate these degradation phenomena, three-dimensional fluorescence mapping (PLE) spectroscopy was employed as a sensitive tool for monitoring the electronic behavior of Pigment Red 53:1 during and after UV irradiation.

Under pristine conditions, the pigment exhibits a well-defined and intense emission peak at 627 nm, which can be attributed to the stable electronic transition of the intact azo chromophore within the crystalline matrix (Fig. 2).

This band is characteristic of the pigment in its non-degraded state and reflects the electronic stability of the conjugated system.

Following exposure to UV-A radiation (λ = 365 nm), a marked alteration of the spectral profile was observed.

Specifically, the intensity of the 627 nm band decreases significantly, indicating that the original electronic configuration of the chromophore is no longer preserved (Fig. 3).

This decrease in emission intensity is a direct consequence of the cleavage of the azo bond (–N=N–), as well as structural disruptions in the extended conjugation of the pigment molecules, which reduce the efficiency of radiative recombination.

Moreover, the residual fluorescence undergoes a progressive blueshift, shifting towards shorter wavelengths (Fig. 4).

This spectral shift suggests the formation of new emissive states, likely arising from structural rearrangements within the molecular framework and modifications of the local environment in the crystal lattice.

The blueshift is consistent with a reduction in the conjugation length of the chromophore and changes in intermolecular interactions within the pigment lake structure, such as altered coordination with Ba^{2+} ions.

As the degradation process advances with prolonged irradiation, the fluorescence spectra reveal the appearance of an additional band at approximately 490 nm, whose intensity gradually increases (Fig. 5).

This new emission can be attributed to the formation of degradation by-products, including aromatic amines, quinonoid species, and oxidized intermediates.

These compounds exhibit different electronic transitions compared to the intact pigment, giving rise to distinct fluorescence emission.

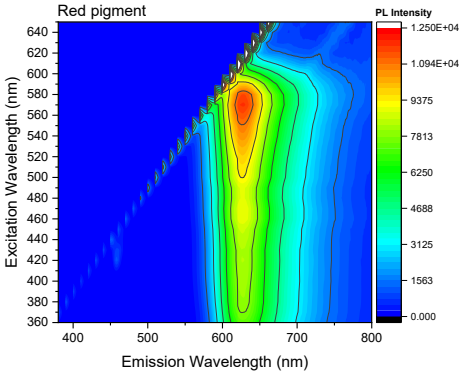


Fig. 2. 3D Fluorescence mapping of red pigment before UV-A irradiation.

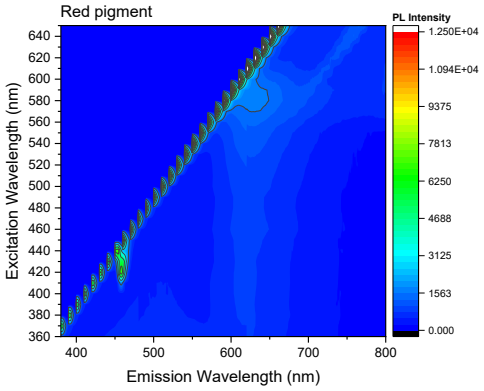


Fig. 3. 3D Fluorescence mapping of red pigment after UV-A irradiation.

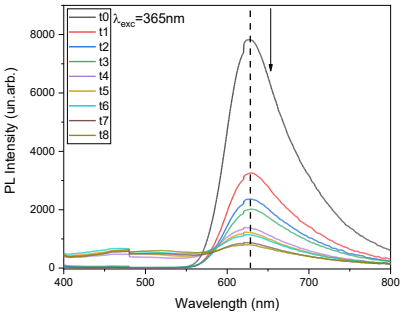


Fig. 4. Fluorescence spectra extracted at different time intervals for λ_{exc}=365nm. Behavior of the peak at 627 nm.

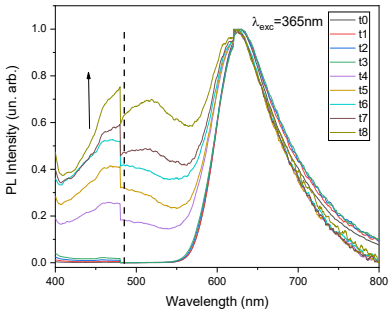


Fig. 5. Fluorescence spectra extracted at different time intervals for λ_{exc}=365nm. Behavior of the peak at 490 nm.

V. CONCLUSIONS

In summary, this work highlights how UV-A exposure can induce complex photo-induced redox processes in red lake pigment, leading to significant changes in its fluorescence behavior. The interaction between light and material can drive both chemical transformations and the formation of new phases, which contribute to the progressive changes in the emission spectrum observed during the aging process.

3D Fluorescence Mapping appears to be a highly effective and sensitive technique for detecting early signs of pigment degradation under UV exposure. This technique allows us to follow in real time how fluorescence changes revealing processes like oxidation or structural changes specific to each pigment.

The method is completely non-invasive and does not require taking samples, making it ideal for use on valuable artworks. Thanks to its ability to monitor materials without causing damage, it offers great potential for preventive conservation and long-term preservation of cultural heritage.

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VI. REFERENCES

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