IN-SITU TECHNICAL STUDY OF MODERN PAINTINGS

PART 2: IMAGING AND SPECTROSCOPIC ANALYSIS OF ZINC WHITE IN PAINTINGS FROM 1889 TO 1940 BY ALESSANDRO MILESI (1856-1945)

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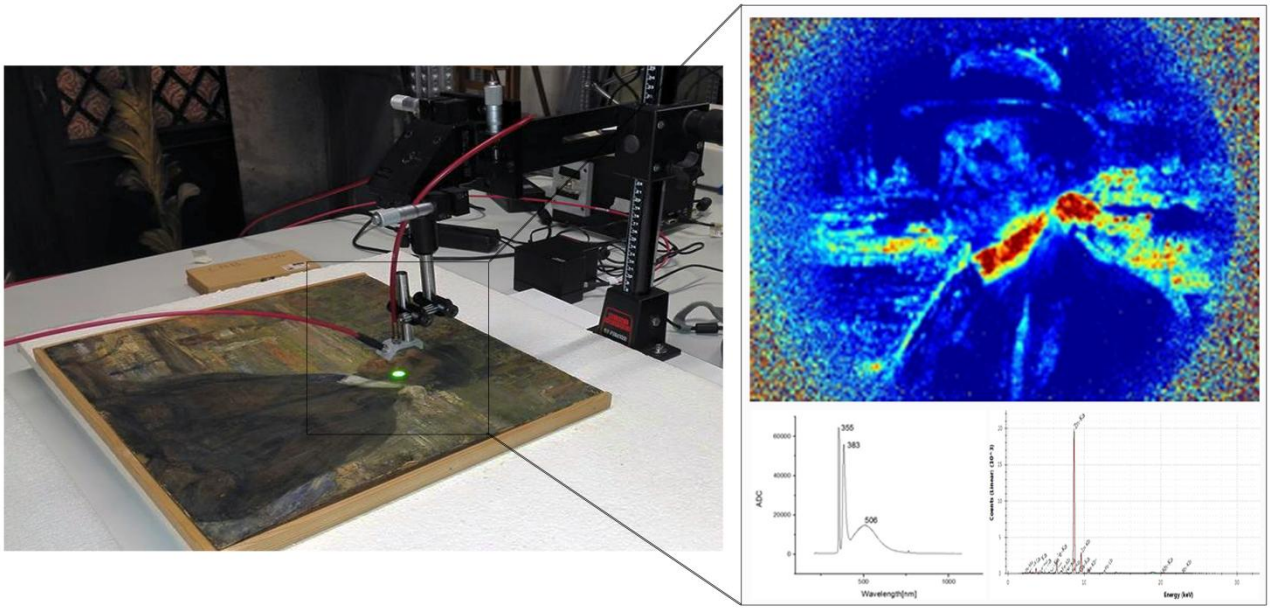
Highlights:

- application of fluorescence spectroscopy and imaging for the mapping of zinc white based in modern paintings

- correlation between differences in emission decay kinetics imaged in paintings linked to different paint formulations containing Zinc white

Graphical Abstract



Abstract

We present a multi-analytical in situ non- invasive study of a series of emblematic paintings by Alessandro Milesi (1856-1945) from the collection of the International Gallery of Modern Art Ca' Pesaro in Venice. Eight paintings dated from 1897 to 1910 were studied with imaging and spectroscopic techniques. White pigments were characterised by a combination of X-ray fluorescence spectroscopy which traced the presence of zinc-based pigments in Milesi's paintings, Raman Spectroscopy, Laser Induced Fluorescence (LIF) Spectroscopy and Time-resolved Luminescence Imaging. Time-resolved analysis of luminescence emissions revealed the nanosecond emission from organic compounds and the slower emission from the luminescent inorganic pigment Zinc Oxide that varied between 1.1 and 1.6 microseconds. In this work, data regarding the distribution of luminescent pigments was acquired with a time-gated imaging detector. Furthermore, differences in emission decay kinetics recorded from different paintings can be ascribed to different paint formulations or origins of the Zinc white in paint.

Keywords:

in-situ analysis, non-invasive spectroscopic techniques, Time-Resolved Luminescence Imaging, LIF (Laser Induced Fluorescence), Zinc oxide, Alessandro Milesi

1. Introduction

In this work we present a method based on the integration of complementary spectroscopic and advanced imaging techniques for the analysis of eight paintings by the Venetian painter Alessandro Milesi (1856-1945) from the collection of the International Gallery of Modern Art Ca' Pesaro in Venice. X-ray fluorescence spectroscopic analysis, luminescence spectroscopy and time-resolved luminescence imaging were used for the mapping of emissions from the painting surface [1]. Research on impressionist paintings by Vincent Van Gogh has reported the long-lived luminescence ascribed to Zinc-based white pigments [2]. Other complementary research on micro-samples has suggested that different paint tubes have different luminescence signals with emissions decaying on the microscale [3], and that the composition of zinc white paints produced during the 19^{th} c. varies greatly [3,4].

The pigment zinc oxide was first marketed in 1834 by Winsor & Newton (UK) under the name "Chinese White". The mineral Zincite (Zn,MnO) was not used for the production of the pigment because of the impurities of iron and manganese that are responsible for its reddish colour [5,6] . There are three main methods for obtaining Zinc Oxide : a so-called French (indirect) and American (direct) processes, and the wet process.

In the indirect or French method, developed between 1840 and 1850, the initial sublimation of metallic zinc in clay (or cast iron) crucibles occurs at a temperature between 1230-1270 °C. When the crucible is exposed to the air, the greenish-white molten zinc oxidizes, giving rise to a white cloud, that is then cooled to below 100 °C [7]. In the second direct or American method, zinc-containing minerals such as Franklite($(Zn^{2+}, Mn^{2+}, Fe^{2+})(Fe^{3+}, Mn^{3+})_2 O_4$), Willemite($Zn_2SiO_4$) , Sphalerite (ZnS) and Zincite (Zn,MnO) are mixed with charcoal and smelted in the presence of air (oxygen). The process is followed by the re-oxidation of zinc, as in the indirect method [8]. However, unlike the indirect method, in which finer and

purer particles are formed, in the American method the resulting zinc oxide presents many impurities. These include dust, residues, soot, and different metal oxides [9]. In the third wet process solutions of $ZnSO_4$ or $ZnCl_2$ are used to precipitate $ZnCO_3$, which is calcined to yield ZnO. Recent studies have shown that zinc oxide in the presence of drying oils can catalyze cross-linking processes and leading to the formation of rigid and fragile films [10]. Zinc oxide reacts with fatty acids in binding media to form basic soaps such as zinc carboxylates [11-14].

The purpose of this work is to investigate the luminescence of Milesi's paintings and to map the presence of the luminescence as a function of lifetime using Time-resolved photoluminescece imaging (TRPL). TPRL is based on the measurement of the temporal properties of the fluorescent emission, mapped in every pixel of an image, and the reconstruction of a lifetime image of the region analyzed. The luminescence decay kinetic associated with organic molecules tends to be on the order of picoseconds or nanoseconds [15] and may be affected by a number of factors such as pH, temperature, solvent polarity. The visible broad emissions from organic materials cannot generally be used for their identification. A different decay behavior is detected in luminescent inorganic materials typically present in modern paintings. Semi-conductors, such as Cadmium and Zinc-Based pigments, are typically characterized by a rapid picosecond band gap emission at well-defined wavelengths, that occur following the recombination of an electron with a hole from the conduction to the valence bands[16,17]. In addition, trap state levels, present in these emitting molecules as a consequence of intrinsic and extrinsic defects in semi-conductors, give rise to further radiative relaxation decay paths with much longer temporal scales on the order of microseconds[18].

2. Materials and methods

2.1 Case studies

Eight painting by Alessandro Milesi (1856-1945) from the collection of the International Gallery of Modern Art Ca' Pesaro in Venice and dated from 1889 to 1940s, were studied. All paintings are reported in the General Catalogue as being in oil on canvas or cardboard.

2.2 In-situ analysis

In order to better understand materials that give strong emissions recorded in UV Photography, X-ray fluorescence spectroscopy was used for the elemental analysis of different points on the surface of the paintings. This was followed by Laser Induced Fluorescence (LIF) spectroscopy on spots of the painting. Time-resolved Lifetime Imaging was carried out on specific areas of each painting. Results of analysis are summarised in Table 1.

Table1: Summary of results from the study of paintings by Alessandro Milesi . Different points were analyzed by X-ray Fluorescence (XRF), and main and trace (tr) elements are indicated. Luminescence emissions were measured with Laser Induced Fluorescence (LIF) spectroscopy and the band gap is ascribed to ZnO and trap states. Results from Time-Resolved Luminescence Imaging (TRPL-imaging) allow the calculation of effective lifetime on the ns-time scale, based on the bi-exponential fitting of the luminescence emission as a function of time.

Painting	Date	Size (cm)	Inventory #	Support	Analyzed area	Main elements identified with X-ray Fluorescence Spectroscopy	Laser Induced Flurescence Emission/nm	Calculated lifetime from TRPL-imaging /ns
Puttino	1897	46x28	1909- Cl. I n. 1966	canvas	Face	Zn, Pb, S	384 (ZnO)	1500
Ritratto di signora	1897	79x 64	2171	canvas	Face	Zn,Pb, Fe, S	382(ZnO)+507	1400
Ritratto del maestro Antonio Acerbi	1898	49x39	2062	canvas	collar/background	Zn, Ca, S (collar) Zn, Ca, Pb(tr) (Background)	382(ZnO)+470+586	1650
Ritratto di Lorenzo Perosi	1899	55x40	1930 Cl. I n. 2003	canvas	Face	Nd	382(ZnO)+507+616	1575
Ritratto di Luigi Luzzati	1912	34x23	1956 Cl. I n. 1958	cardboard	Face	Zn,Pb,Fe, S, Ca(tr)	382(ZnO)+517	1110
Ritratto di Luigi Luzzati	1912	66x47	2348	canvas	Face	Zn, S, Fe, Co, Ca(tr) Zn,Cr,S,Pb(tr),Fe(tr)	384 (ZnO)	1500
Ritratto di John Lavery	1912	36x41,7	0619	cardboard	Face	Zn, Pb, Fe, S, Ca	384(ZnO)+505	1100
Paesaggio con contadina	1940	31,5x41	3924	cardboard	Sleeve, cow and wheel	Ba, Cd, Pb, Zn, Fe, S, Ca (sleeve) Ti, Ba, Cd, Pb, Zn (cow) Ti, Ba, Cd, Pb, Zn, Co (wheel)	382+447+498+567	1500

2.2.1 X-ray Fluorescence Spectroscopy

X-ray fluorescence (XRF) spectroscopic analysis was carried out with a compact, portable and high-performance XRF spectrometer (ELIO produced by XGLal srl/Bruker). For this work, the excitation source works with a Rh anode, the X-ray beam is collimated with a diameter on the paint surface of about 1.3 mm. XRF measurements have been carried out by fixing voltage at 50 and 15 kV exploring a field of analysis from 1 to 40 keV [19].

2.2.3 Laser Induced Fluorescence spectroscopy

Laser Induced Fluorescence (LIF) has received significant attention for the analysis of pigments and binding media, but is intrinsically limited as a diagnostic tool [20, 21]. Laser excitation has distinct advantages over lamp illumination, such as brightness and monochromaticity, which allow fluorescence measurements without the need for filters to remove stray or parasitic blue radiation. In this work excitation at 355 nm was provided by the third harmonic of a Q-switched Nd:YAG laser, with 10 ns pulse duration (Spectron Laser Systems); a maximum of 300 pulses and fluence of 5mJcm^{-2} per pulse were used [18]. Detection of luminescence was carried out by coupling a compact spectrometer (TM-CCD C10083CA-2100, Hamamatsu Photonics) (range 320–1100 nm with a spectral resolution of 6 nm) to fibre optics [17].

2.23. Time-resolved luminescence Lifetime Imaging

A time- gated intensified camera(C9546-03, Hamamatsu Photonics, Japan), capable of an acquisition gate with a temporal width adjustable from 3 ns to continuous mode, is used to measure the nanosecond, microsecond, or millisecond kinetics of the luminescence emitted in each point of the surface of interest immediately following pulsed excitation. UV excitation was provided by a frequency- tripled diode- pumped Nd-Yag laser (FTSS 355-50, Crylas GmbH, Germany), emitting 1 ns pulses at 355 nm. The laser beam was magnified with suitable optics in order to uniformly illuminate a circular area close to 25 cm in diameter, leading a typical fluence per pulse kept below 140 njcm^{-2}.By using a time-gated ICCD camera and proper

electronic synchronization, images were recorded at different delays with respect to laser pulses [2] . Imaging data was mathematically fit using a bi-exponential decay at delays from 1-2000 ns to model both the short and long-lived emissions.

3. Results and discussion

3.1 Elemental Analysis with X-ray fluorescence spectroscopy

X-ray fluorescence spectra reveal the bulk composition of paint and give results give rapid and important insights regarding the paints used by Milesi. The white pigments found in paintings are rarely pure, with the exception of the ZnO found in “Ritratto del maestro Antonio Acerbi”. XRF spectra reveal mixtures of varying concentrations of Zinc together with Lead, as well as elements which can be ascribed to other pigments. In the canvas painting of “Ritratto di Luigi Luzzati“ there is a high concentration of Sulphur which could be related to the presence of ZnS as well as ZnO, but no Barium is found, thus excluding the presence of lithopone (a coprecipitate of ZnS and $BaSO_4$). Similarities between XRF spectra can be appreciated in Figure 1.

The distinction between contamination from other pigments, the presence of elements due to additives and dryers in paint formulations and various impurities specifically associated with the Zinc white pigment is complex, and secure identification of elements related to the production of the white pigments would normally require microscopic analysis and sampling [4]. It is nonetheless useful to compare results from XRF spectra, especially for the presence of trace Cd, which can be associated with the French process of production of the pigment, while the absence of Cd could be linked to the wet process of synthesis. Very similar compositions are found between “Ritratto di Luigi Luzzati“ canvas and "Ritratto di John Lavery”, with slight differences detected in XRF spectra , each containing contributions from Zn, and weaker signals from S , Ca, and traces of Cd. “Puttino” and “Ritratto di Lorenzo Perosi” are also similar in composition,

each containing a mixture of Zn and Pb, together with traces of Cd, Cr and Fe. “Ritratto del maestro Antonio Acerbi”, by contrast contains mostly Zn, and presents only traces of Pb, Cd and Cr (traces are not visible in XRF spectra presented in Figure 1 but are appreciable on the logarithmic scale).

Figure 1: Comparison of X-ray Fluorescence spectra recorded from different areas of white paint used by Alessandro Milesi in paintings (see Table 1). Groups are based on similarity and the presence of principal emissions from Zn, Pb and Fe. Emissions from trace elements are not visibile in these spectra presented with linear scale of intensity, normalised to the emission from Zn..

3.2 Laser Induced Fluorescence (LIF) spectroscopy

Laser induced fluorescence spectroscopy reveals the presence of zinc white in many but not all of the paintings studied (Figure 2). The near band edge (NBE) transition at approximately 380 nm, together with blue luminescence (BL) between 400-500 nm and the green luminescence between 500-550 ascribed to trap states (TS) were observed in varying intensities in different paintings. Recent research on historical ZnO has reported the band gap and shallow trap states contribute to the NBE emission between 380-390 nm [17,23]. The NBE emissions reflect differences (Figure 2) in the concentration of shallow trap states that give rise to a red shift emission centred at 385 nm, a well-known phenomenon for semiconductors. However, the intensity of the emission from TS depends on fluence and the differences observed may be due to slight differences in power density of laser excitation at the paint surface during measurments, with greater power favoring trap state emissions. The variation in emission spectra observed in paintings could also be influenced by different formulations of ZnO paint.

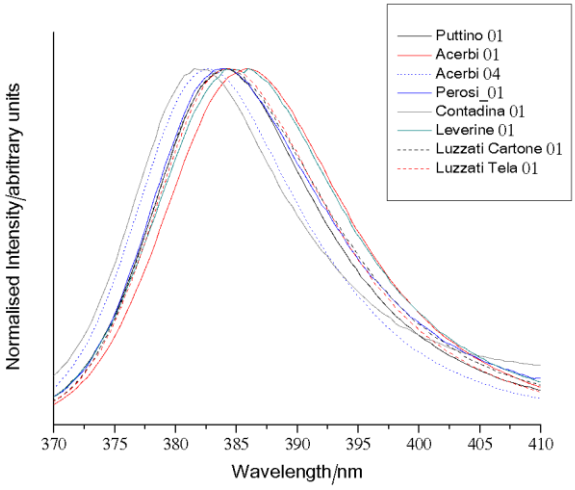


Figure 2: Laser Induced Fluorescence spectra showing the variation in the position of the near band edge (NBE) and blue luminescence (BL)

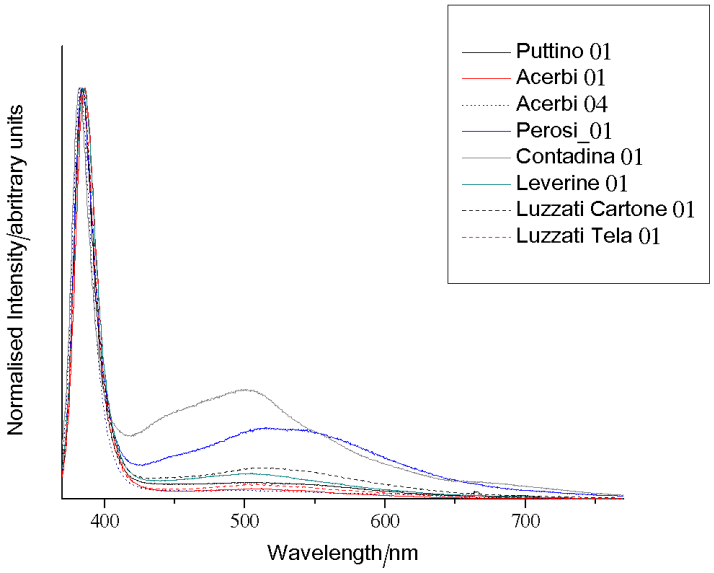


Figure 3: Laser Induced Fluorescence spectra demonstrate significant differences in the green emission from white areas recorded from different paintings. Spectra are shown normalised to the emission between 380-390 nm for clarity

The green emission centred between 500-550 nm observed in LIF spectra varies in intensity and position, and can be ascribed to different surface trap states in ZnO (Figure 3). The emission in ZnO is highly sensitive to binding media, and the formation of complexes may lead to greater Zn vacancies and modify the intensity and lifetime of trap state emissions. The formation of carboxylates likely results from the leaching of Zn into binding media, resulting in the increase in the concentration of vacancies on the surface of ZnO

particles, but pure zinc carboxylates are not known to yield luminescence [22, 23]. Nonetheless, while LIF spectra suggest differences in the ZnO present in different paintings, it is not straightforward to correlate these differences with specific formulations of ZnO.

3.3 Time resolved Lifetime Imaging

The fluorescence detected by LIF is due to contributions from the band gap at 380 nm and to TS which give rise to a green-coloured emission. TS are responsible for the long lived luminescence recorded with time-resolved imaging. The average kinetics of emission vary in different paintings; Zinc white from the paintings of Lavery and Luzzati (both 1912) have the most rapid decay, while paintings of Acerbi and Perosi (pre 1900) have the slowest. Other paintings give rise to an intermediate luminescence decay. The calculated lifetime values can be related to pigment production processes, and it is believed these are most related to the different types of grinding zinc oxide by wet and dry processes.

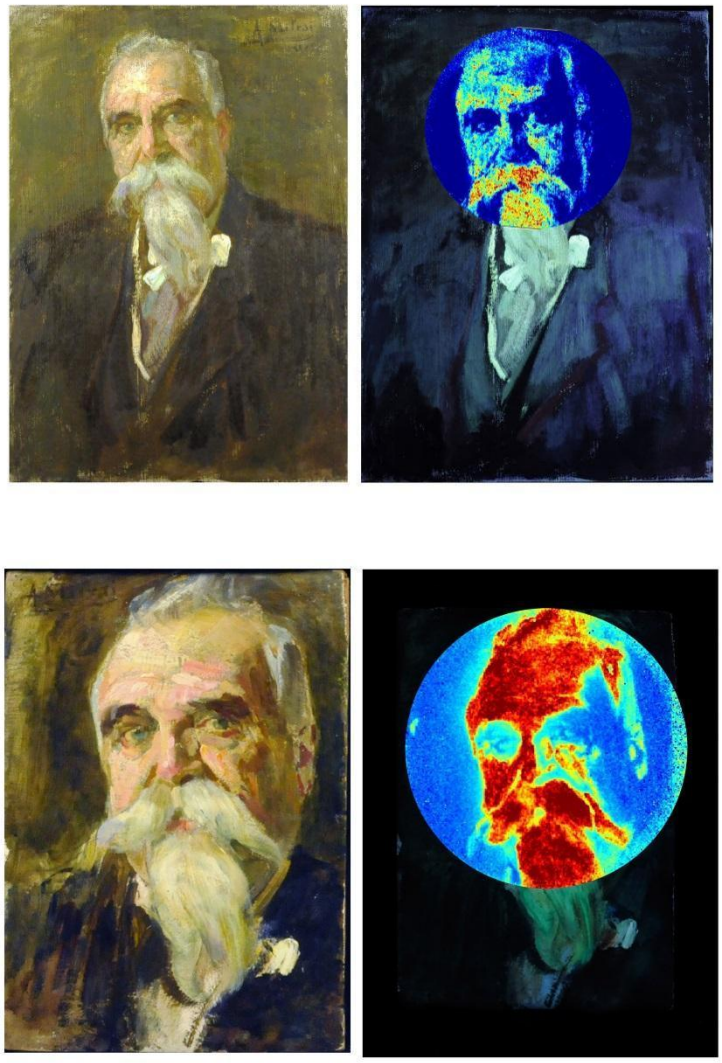
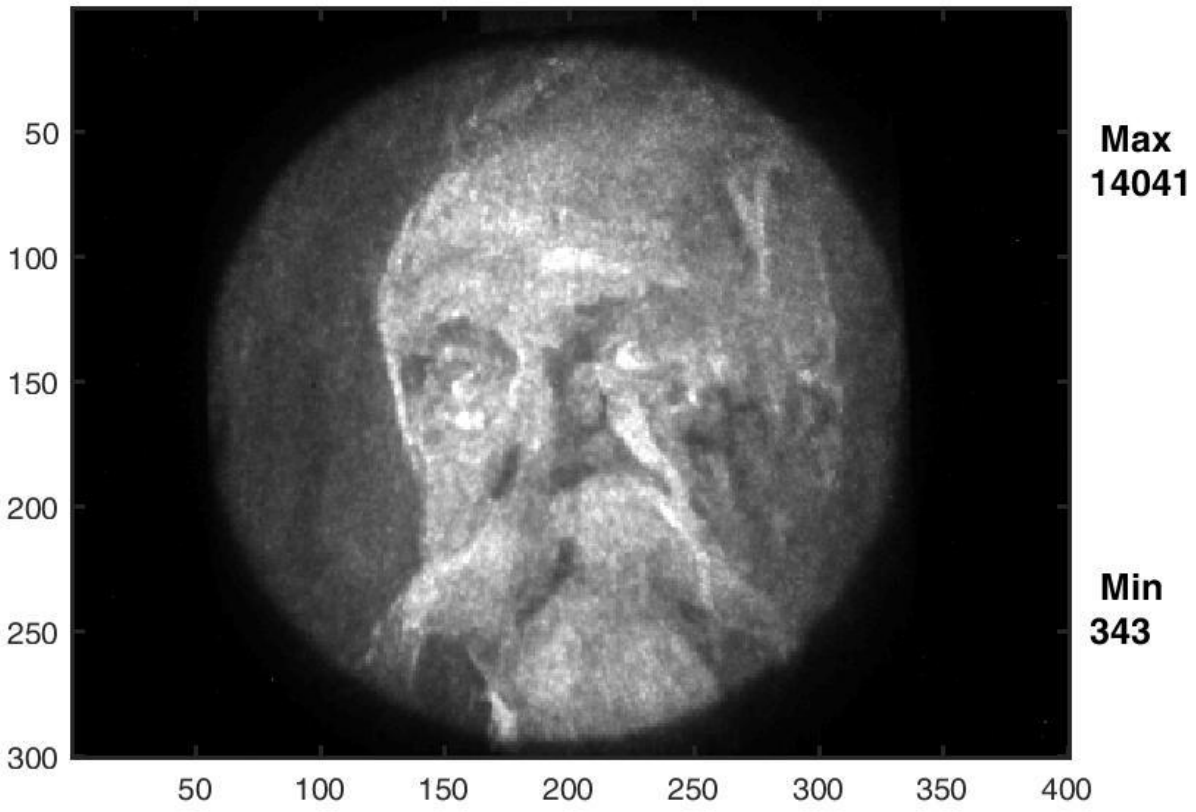


Figure 4: A comparison of paintings with results of Time-resolved luminescence images in false colour with long-lived emissions in red that are ascribed to trap-states in ZnO, present in the flesh tones and background in "Ritratto di Signora", and in the highlights in the canvas painting and the sketch on cardboard of "Ritratto di Luzzati".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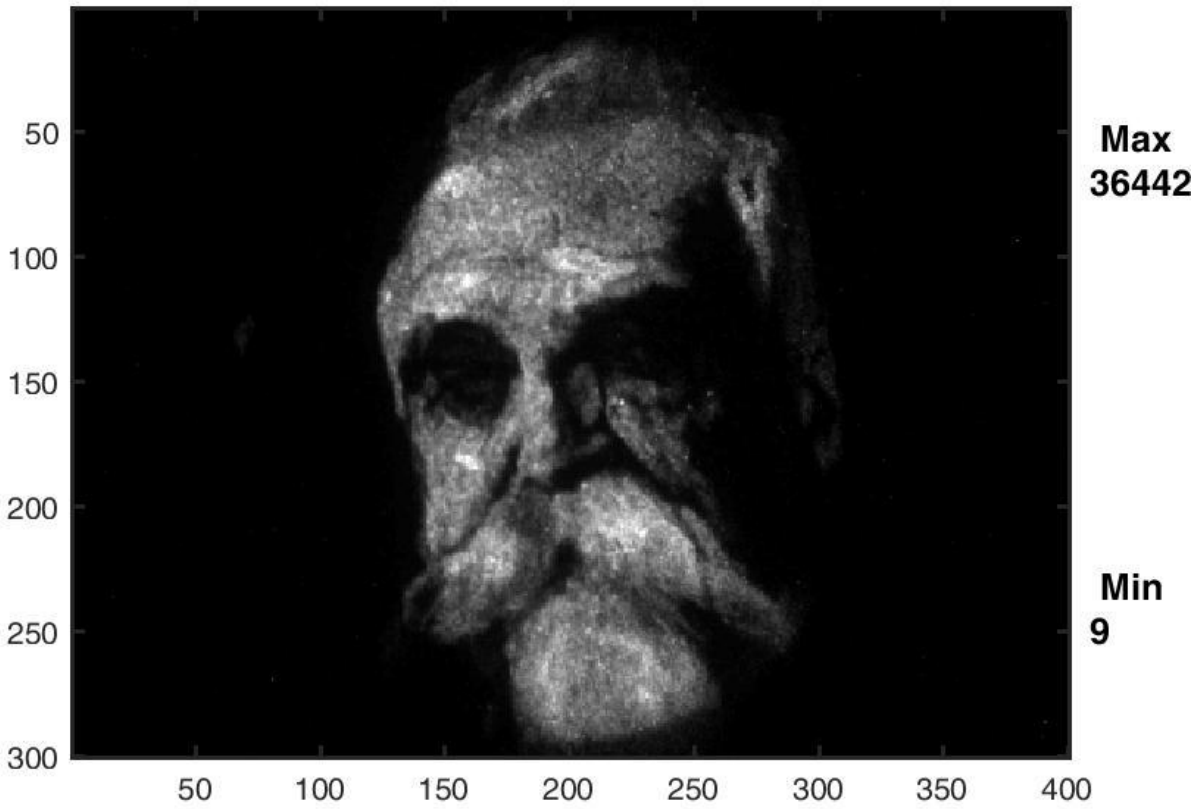

Figure 5: Gated images acquired from the same painting of "Ritratto di Luzzati" on cardboard at 0 ns (top) vs. 10 microsecond delay (bottom). These images are particularly useful to map the presence of zinc white, seen most clearly as intense signals at longer delays.

Data from time-resolved luminescence imaging provides profiles of the decay kinetics averaged between 400-700 nm, which corresponds to the trap state emission. By focusing our attention on the long-lived emission in ZnO we model the luminescence lifetime of trap states emitted from paintings, as listed in Table 1. The long emission from trap states in ZnO varies in lifetime from 1100 ns in Levery to 1800 ns in paintings of Acerbi and Perosi. These lifetime values are below those detected with spectrally resolved gated luminescence measurements in model samples and historical pastels but are on the same order of magnitude [17]. It has been suggested that trap state emissions may also decrease in lifetime following complexation of ZnO [23].

4. Conclusions

Results from analysis of paintings by Milesi suggest that Time resolved Luminescence imaging is a powerful technique for the imaging of the presence of long-living emission which in this work can be ascribed to Zinc white. Variations in the composition of the paint used by Alessandro Milesi are reflected in the different luminescence lifetimes calculated from different paintings. By using a gated detection system it is possible to differentiate rapidly the emissions from organic binding media from those associated with trap states in the semiconductor pigments. Complementing data from elemental analysis and laser-induced fluorescence spectroscopy, lifetime maps allow a better understanding and visualisation of the way that Milesi painted, how he used zinc whites to apply highlights and how different paints containing differently prepared zinc oxides may have been used during his career. These methods could be extended both to the study of other paintings and, in combination with microscopic analysis, could be employed for the analysis of paint microsamples, pigments and cross-sections.

A**cknowledgments**

The authors thank the MUVE (Fondazione Musei Civici-Venice) for providing the access to the collection of the International Gallery of Modern Art "Ca' Pesaro".

This research was possible thanks to the financial support from Ca' Foscari University of Venice "Premio Giovani Ricercatori" (Prize for Young Researchers) .

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