On the discovery of an unusual luminescent pigment in Van Gogh's painting "Les bretonnes et le pardon de pont Aven"

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Abstract Spectrally and lifetime-resolved UV-induced luminescence imaging have been applied to the in situ analysis of Vincent Van Gogh's painting on paper "Les bretonnes et le pardon de pont Aven". The in situ investigation revealed the presence of an unusual microsecond green emission from the white painted areas of the watercolour, and this long-lived emission has not been reported in modern paintings by other authors. In order to attribute and suggest an identification of the luminescent pigment, our analysis was integrated with further measurements on commercially available modern white pigments (zinc white, Lithopone white, Blanc Fixe, zinc sulphide, and copper-doped zinc sulphide) and with an in-depth study of the synthesis processes of zinc-based pigments available at the end of the 19th century. Analysis suggested an attribution of the unusual emission from the Van Gogh painting to a particular variety of zinc sulphide pigment, characterized by the presence of copper impurities which were unintentionally introduced in the crystal matrix during its production. The present study is the first application of lifetime imaging for the mapping of long-lived luminescence from the semi-conductor pigment.

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1 Introduction

Modern painting is part of a larger movement that encompasses all art forms and which is generally thought to have originated in the mid 1800s. In its application to painting, the movement spanned the careers of many well-known artists including Van Gogh, Monet, Cezanne, Gauguin, Picasso, and Matisse, all of whom experimented with new ways of seeing and fresh ideas about the nature of materials and functions of art [1].

If modern paintings are much better documented than traditional artworks, often thanks to well-preserved letters and technical notes by the artists themselves, from a material point of view modern paintings are frequently made of compounds, media, and pigments which are extremely difficult to characterize. Indeed, the social transformation brought by the Industrial Revolution triggered the emergence of new ideas in all areas including fine art, where new materials (such as synthetic pigments and organic dyes, polymeric

paint media, and industrial canvasses) and new application techniques were freely tested by artists.

Focusing on newly synthesized inorganic pigments, the 19th century was a period of huge change for painters. New colors and enhanced versions of established pigments were introduced with bewildering regularity every few years. For example, it is noteworthy that at least three different zinc-based white pigments (zinc oxide, zinc sulphide, and Lithopone) became available in the same period and that for each one of these pigments, more than ten known patents were registered. In addition, in 1841 the American painter John Rand patented the first collapsible tin paint tube that revolutionized the color palette and technique of plein-air painters by offering them a range of premixed colors in a portable medium [2].

Undoubtedly, the vast range of innovative materials used by artists significantly compromises the conservation of works of art, mainly because their long-term behavior, and the effects of ambient degradation is little understood. In recent years, however, there has been a growing number of studies on modern paintings and related paint materials: for example, the use of complex laboratory techniques, such as synchrotron radiation and electron energy loss spectroscopy, has allowed the elucidation of the degradation paths of some inorganic pigments, as can be inferred in works from Van der Snickt [3], Monico [4, 5], and Casadio et al. [6], which focus on the degradation process of cadmium and chromate pigments in valuable modern artworks. In a completely different application, synchrotron-based X-ray fluorescence spectroscopy allowed the discovery of a lost painting by Van Gogh [7]. In turn, the employment of simpler, but still effective invasive and noninvasive spectroscopy devices permitted the identification of some of the inorganic pigments employed in modern paintings [8–11], including works by Cezanne and Renoir.

The materials of modern art pose problems that in many cases make the non-invasive approach mandatory. In fact, due to the good condition of many examples of modern paintings, sampling opportunities are in general limited and, indeed, seldom allowed. Moreover, due to the difficulties in the transport or movement of paintings (due either to insurance costs or fragility), there is an increasing demand for the engineering of mobile instrumentation. In this perspective, portable imaging devices can be particularly helpful: for example, the presence of degradation phenomena of cadmium-based pigments in paintings by James Ensor was made possible by simply employing UV-induced luminescence imaging [3]. Multispectral cameras, sensitive in the visible and in the near-infrared spectral range, have been shown to be particularly helpful for the identification of pigments on paintings by Van Gogh and Picasso [12, 13]. Finally, even though still not used for the analysis of modern works of art, a recently developed EDXRF imaging portable

Fig. 1 Color image of the Van Gogh watercolor "Les bretonnes et le pardon de pont Aven," at the Modern Art Gallery (Galleria di Arte Moderna), Milan, © Galleria di Arte Moderna 2011

device [14] could be invaluable for the identification of modern paint materials.

In this context, our research group was involved in the study of one of the few paintings from Vincent Van Gogh located in Italy. The study was conducted with the aid of in situ luminescence spectroscopy imaging analysis, and no sampling from the painting was allowed. In situ measurements, which revealed the presence of a luminescent white pigment, were integrated with laboratory analysis on model paint samples in order to provide a better understanding of the artistic materials employed by the artist.

2 Materials and methods

2.1 The Van Gogh watercolor

"Les bretonnes et le pardon de pont Aven," also known as "Breton Women (after Emile Bernard)," is a watercolor painted by Vincent Van Gogh in Arles on December 1888 and currently located at the Modern Art Gallery in Milan (Italy). The watercolor (74 × 60 cm in size, shown in Fig. 1) is actually a copy of a painting by Emile Bernard, "Breton Women in the Meadow (Le Pardon de Pont-Aven)." The Dutch artist, impressed by the original way of painting of his young friend Bernard, quickly prepared and sent a copy of the painting to his brother Theo [15], to show him the new stylistic forms employed by Bernard, which include the lack of perspective, the original use of bright colors and the need for simplifying shapes against flat backgrounds. It is not completely clear if Van Gogh painted the watercolor for sale or just as a way of informing his brother, and this consideration should be taken into account in an assessment of the quality of the paint materials employed by the artist.

2.2 In situ imaging spectroscopy devices

In situ investigations of the painting were conducted with two different portable luminescence imaging devices, aimed at measuring both the temporal decay and spectral properties of the UV-induced luminescence emitted from the surface. Details of the two devices are described elsewhere [16, 17] and are only summarized here.

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 kinetic of the luminescence emitted in each point of the surface of interest immediately following pulsed excitation. UV excitation is 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 is magnified with suitable optics in order to uniformly illuminate a circular area close to 25 cm in diameter, leading to a typical fluence per pulse kept below 140 nJ cm^{-2}. The kinetic of the emission is reconstructed by recording its intensity at different delays with respect to excitation pulses by employing a home-made trigger electronic device and a digital delay generator (DG535, Stanford Research Systems, USA). The temporal jitter of the whole device is close to 0.2 ns.

A multispectral camera, sensitive in the visible spectral range, is used to record luminescence spectral information. The detector is made of a low-noise, black and white CCD camera (Retiga2000, QImaging, Canada) coupled to a band-pass liquid crystal tunable filter (Varispec, CRi, USA). Luminescence excitation is provided by two properly filtered UV lamps ($\lambda_{exc} \approx 365$ nm), placed approximately at 1 meter from the painted surface, leading to a typical mean irradiance of 200 µW cm^{-2} on the analyzed surface. The measurement protocol involves the acquisition of 33 luminescence images from 400 to 720 nm in 10-nm steps, allowing one to estimate the spectral shape of the luminescence emission in each point of the field of view after proper correction for detection efficiency.

The multispectral camera is used for recovering diffuse reflectance spectra from the painting [18]. Two voltage-stabilized 150 W tungsten halogen lamps (DLH4, Dedotec, USA) are employed for illuminating the painted surface. In this case, the measurement protocol involves the acquisition of 65 images from 400 to 720 nm in 5-nm steps. Proper calibration with a white balance paper (GretagMacbeth ColorChecker White Balance) and a 99% Diffuse Reflectance Standard (SphereOptics, USA) allows the estimation of the reflectance factor $\rho_{x,y}(\lambda)$ in each point of the field of view. For the present study, reconstructed diffuse reflectance spectra are employed in order to take into account modifications to luminescence spectra induced by the selective absorption of coloring absorbing pigments [19, 20], as will be better explained in Sect. 2.4.

## 2.3 Modern white paint samples and laboratory equipments

Four inorganic white pigments, synthesized in the 19th C. before 1888, were selected for the present research, namely zinc white (pure ZnO), Lithopone white (∼60% ZnS and ∼40% BaSO$_4$), and the two main components of Lithopone pigment, *Blanc Fixe* (∼99% BaSO$_4$) and zinc sulphide (pure ZnS). All pigments were purchased from Kremer (Kremer Pigment GmbH, Germany) and prepared as model paint samples by dispersing them to Arabic gum and spreading them as single-layer thin films onto silica substrates.

A further white pigment, actually not available as a pigment at the time of Van Gogh's life, but nowadays well known for its luminescence properties, was selected for the present research: the pigment, known as Luminescent Green, is made of copper-doped zinc sulphide (ZnS:Cu); it was purchased from Kremer, mixed with *Blanc Fixe*, and prepared as a thin paint sample in the same way of the other pigments. The estimated thickness for all paint films is close to 50 µm.

The prepared samples were characterized in laboratory with the following techniques:

1. *UV-VIS emission spectroscopy*: A bench-top spectrofluorimeter (Fluorolog 2-1, Horiba Jobyn Yvon) with front face (23°) detection was employed for estimating the emission properties of each sample. Fluorescence excitation emission spectra (EES) were constructed by scanning emission spectra from 350 to 600 nm as functions of excitation wavelength from 300 to 420 nm. The detected signal was corrected for excitation and detection efficiency.

2. *Nanosecond time-resolved emission spectroscopy*: A time-gated visible spectrometer, with sensitivity in the 370–650 nm spectral range, was employed for estimating the nanosecond emission decay kinetic of each sample as a function of the emission wavelength [16]. The spectrally and lifetime-resolved device is based on a time-gated detector coupled to a visible spectrometer. UV-pulsed excitation (at 355 nm) was provided by the same Nd–Yag laser employed in the in situ measurements, whereas the time-gated detector is a linear ICCD characterized by a fixed gate width of 10 ns, which allows one the assessment of only the nanosecond emission of a sample disregarding slower kinetic components. Even in this case, the temporal jitter of the device is close to 0.2 ns.

3. *Time-resolved imaging*: The time-gated image detector, already employed for the in situ measurements, was used in the laboratory in order to characterize slower (microsecond and millisecond) kinetic components of the selected pigment samples. Depending on the decay kinetic, the camera gate width was set to 100 ns or to 10 µs.

Fig. 2 (**a**) Reconstructed map of the RGB color of the luminescence emission from the Van Gogh painting, following UV excitation ($\lambda_{\text{EXC}} \sim 365$ nm). (**b**) Emission spectra registered from areas 1 and 2 (5×5 mm^2 in size) of the painting; for clarity, the spectrum from area 2 has been multiplied by a factor of 5

a

b
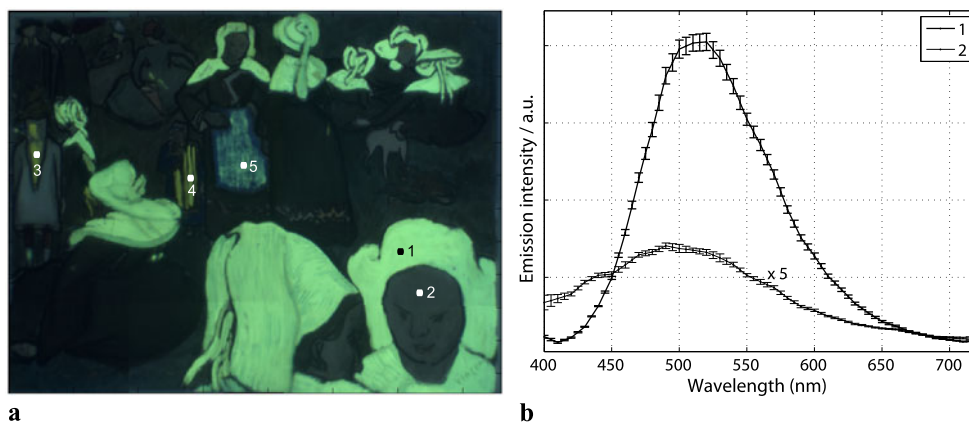
2.4 Data analysis

Analysis of luminescence time-resolved imaging data implies the reconstruction of the effective lifetime map $\tau(x, y)$ in each point of the field of view assuming a simple mono-exponential decay, as already proposed in a previous publication [16].

In addition, time-resolved data from selected regions of the field of view or acquired with the nanosecond time-resolved spectrometer have been analyzed assuming multi-exponential decay models with a maximum of three components on the basis of nonlinear least squares fitting methods [21]:

$$f(t) = \sum_{i=1}^{3} A_i \exp(-t/\tau_i) \tag{1}$$

τ_i and A_i being respectively the lifetime and the intensity at the beginning of the emission for each decay component. In order to take the relative weight of each component into account, the number of photons emitted by each decay component during the whole emission decay was calculated according to the following equations:

$$\int_0^{+\infty} A_i \exp(-t/\tau_i) \, dt = A_i \tau_i \tag{2}$$

$$A_i \tau_i \% = \frac{A_i \tau_i}{\sum_{k=1}^{3} A_k \tau_k} \tag{3}$$

In the text results from multiexponential data analysis are listed as lifetime values and ($A\tau\%$) relative weights.

Precision in the reconstruction of the decay kinetic parameters of the emission mainly depends on the temporal jitter of the time-gated devices and on signal-to-noise ratio. In the present study, decay kinetic values fitted with the employed linear and nonlinear procedures are characterized by a relative standard deviation minor than 5% for repeated measurements. It is noted that the recovered parameters depend on the choice of the fitting procedure and of the sampling scheme. Indeed, the kinetic of complex systems

shows a multiplicity of exponential components, or even a continuous of exponential decays. In such a condition, there is no practical way to measure the exact decay parameters and the choice of a mono-, bi-, or tri-exponential model leads to unavoidable approximations. Nevertheless the estimated decay parameters (lifetime and amplitude) reconstructed with the imaging device have the great advantage of showing, with high reproducibility, the spatial variations of the surface under investigation. In turn, very reliable comparisons can be performed amongst measurements on different samples performed in the same experimental conditions.

Luminescence spectral data registered with the multispectral camera from colored areas are corrected for possible absorption phenomena induced by surrounding colored particles. According to a proposed correction model based on the Kubelka–Munk theory for nontransmitting surfaces [19], corrected luminescence spectra $I^{\text{CORR}}(\lambda)$ are obtained from measured ones, $I^{\text{MEAS}}(\lambda)$, taking into account the diffuse reflectance factor $R(\lambda)$ at all emission wavelengths and at the excitation wavelength λ_{EXC}, as stated by the following equation:

$$I^{\text{CORR}}(\lambda) = I^{\text{MEAS}}(\lambda) \times \left(1 + \sqrt{\frac{\text{REM}(\lambda)}{\text{REM}(\lambda) + 2}}\right)$$
$$\times \left(1 + \sqrt{\frac{\text{REM}(\lambda) \cdot (\text{REM}(\lambda) + 2)}{\text{REM}(\lambda_{\text{EXC}}) \cdot (\text{REM}(\lambda_{\text{EXC}}) + 2)}}\right) \tag{4}$$

$$\text{REM}(\lambda) = \frac{(1 - R(\lambda))^2}{2R(\lambda)} \tag{5}$$

where $\text{REM}(\lambda)$ is the so-called remission function.

3 In situ analysis of the Van Gogh painting

3.1 The measurement of a long lived luminescent white pigment

The surface of the painting was analyzed with the luminescence multispectral camera by registering spectral emission data on adjacent areas of the watercolor. By employing home-made registration software, adjacent multispectral datasets were mapped together with an affine transformation [22] in order to obtain the luminescence multispectral dataset of the whole painting. Starting from this dataset, a color image of the emission was reconstructed on the basis of the RGB color space (Fig. 2a): the map clearly highlights the presence of a bright green emission in the white headdresses of the Breton women. In terms of spectral shape, the corresponding emission spectrum (Fig. 2b, black line) shows a distinct peak at 520 nm with a full width at half maximum (FWHM) close to 110 nm. In comparison, the emission spectrum from most of the non-white areas of the paintings, such as the one measured from the face of the Breton woman, is much less intense (at least of one order of magnitude) and broader, with a FWHM close to 170 nm (Fig. 2b, green line).

In the past, conservators and conservation scientists have ascribed a UV-induced green emission on a modern painting to the presence of a zinc white pigment [23]. Nevertheless, as will be shown with further analyses discussed in the present paper, care should be taken in making this assumption.

Indeed, the analysis of the kinetic of the emission decay provided more interesting and unexpected results. For these investigations, the gating window of the intensified camera was set to 100 ns, and the emission decay was recorded from 0 to 1000 ns with a variable sampling step. The effective lifetime map of the watercolor (Fig. 3a) indicates that white painted areas, corresponding to the Breton headdresses, are characterized by a long lived emission with an effective decay time close to 1100 ns. In comparison the effective lifetime estimated on the areas of the face is much shorter (220 ns).

The emission decay kinetic from regions (1) and (2) shown in Fig. 3a was analyzed with a multiexponential decay model assuming a maximum of three discrete components. Results of the analysis are provided in Table 1: the emission kinetic from the area of the headdresses is well fitted by an exponential decay with lifetime values close to 3.1 ns (2.5%), 66.8 ns (1.3%), and 1.6 µs (96.2%). In turn, luminescence emission kinetic from the area in correspondence of one of the faces appears to be well fitted by lifetime values close to 2.5 ns (78.5%), 11.6 ns (13.2%), and 1.3 µs (8.2%). In this second case, the microsecond component, which makes only a small contribution to the total emission, is due to the detector noise.
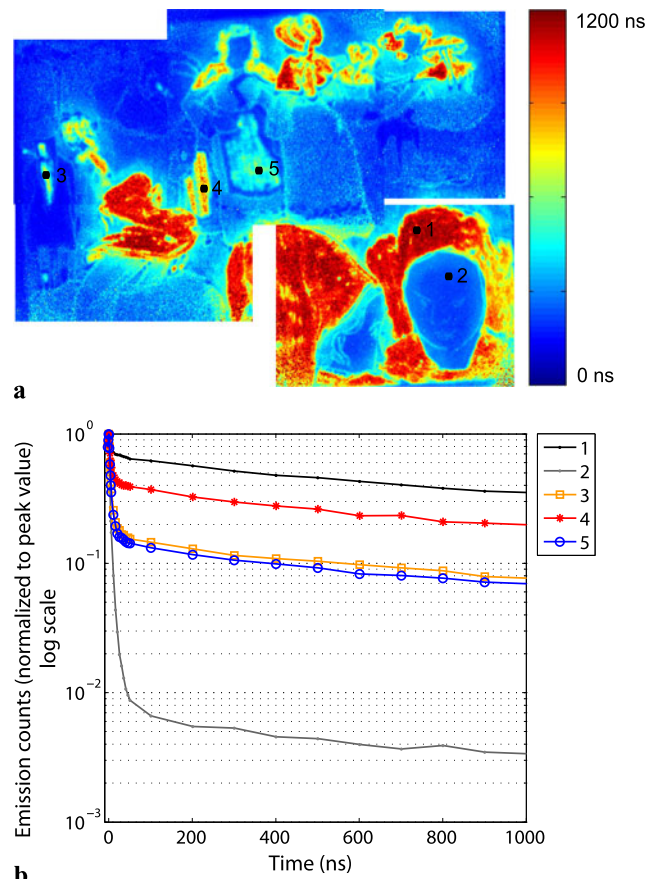
Fig. 3 (**a**) Map of the effective emission lifetime from the Van Gogh painting; the map highlights the presence of a microsecond emission decay from the white painted areas of the painting. (**b**) Emission decay recorded from areas 1 to 5 (5 × 5 mm^2 in size)

Whereas the nanosecond emission registered from the face can be related to the presence of an organic compound with a typical fluorescent nanosecond decay kinetic (possibly ascribable to an organic binder or size, or a protective treatment or the paper substrate), emission from white painted areas is ascribed to a luminescent white pigment characterized by an unusual microsecond lifetime.

3.2 Analysis of other colored areas

Looking back at the reconstructed maps reporting the color and the effective lifetime of the emission from Van Gogh's painting (Figs. 2a and 3a), it is evident that further non-white areas are brightly luminescent and characterized by a microsecond decay kinetic. For example, this is evident for the yellow blond hair of the girl on the left, the yellow stripes of the little boy's clothing and the blue apron of one of the Breton women (areas 3, 4, and 5 in Figs. 2a and 3a).

Related emission spectra and fitted lifetime values are reported in Fig. 4a and Table 1, respectively: in contrast to the white areas, colored areas are characterized by emis-

Table 1 Results of the non-linear fitting procedure on emission decays measured from areas 1 to 5 of the Van Gogh painting by assuming a multiexponential decay model with a maximum of three components. Lifetime values, $A\tau\%$ weights and reduced chi-squared value are reported

	τ_1	τ_2	τ_3	$A_1\tau_1$ (%)	$A_2\tau_2$ (%)	$A_3\tau_3$ (%)	χ^2
Area 1	3.1 ns	66.8 ns	1.6 μs	2.5%	1.3%	96.2%	0.0028
Area 2	2.5 ns	11.6 ns	1.3 μs	78.5%	13.2%	8.2%	0.0141
Area 3	3.7 ns	24.9 ns	1.5 μs	25.1%	2.8%	72.1%	0.0109
Area 4	3.6 ns	91.7 ns	1.5 μs	9.5%	2.0%	88.5%	0.0082
Area 5	3.6 ns	27.4 ns	1.4 μs	32.5%	3.3%	64.2%	0.0111

sion spectra hypsochromically or bathochromically shifted and by microsecond emission kinetics with a minor ($A\tau\%$) weight.

Beside the hypothesis of other long-lived luminescent pigments employed by the artist, it is more reasonable to suppose that these colored areas have been painted with the same luminescent white pigment mixed with nonfluorescing colored pigments. For this hypothesis, the minor weight of the microsecond lifetime can be explained by considering a lower content of the luminescent pigment in the pictorial layer or the presence of absorbing colored particles which partially dampens the emission from the luminescent pigment. In turn, differences in emission spectra should be related to selective absorption phenomena induced by the surrounding colored particles.

In order to understand these absorption phenomena, we tested the correction model described in Sect. 2.4 on emission spectra measured from the luminescent nonwhite areas of the painting. The related diffuse reflectance spectra (Fig. 4b) were retrieved from in situ measurements with the multispectral camera, whereas the diffuse reflectance factor at the excitation wavelength R ($\lambda_{EXC} = 365$ nm) was set to a reasonable value of 0.2 (the effect of the spectral correction is almost unchanged for values of $R(\lambda_{EXC})$ greater than 0.15). From Fig. 4c it is evident that the resulting corrected luminescence spectra much better resemble the one measured of the white headdresses, allowing us to conclude that Van Gogh painted these colored areas by mixing them with the same luminescent white pigment in order to obtain lighter hues.

The indication of the presence of a microsecond luminescent pigment is undoubtedly the most interesting result of our in situ investigations since, to our knowledge, no other work has demonstrated such a luminescent white pigment in modern paintings. Indeed, earth pigments are typically not fluorescent, and nanosecond UV-induced emissions sometimes observed in areas painted with this kind of pigments is related to the employed organic binding medium. In turn, many modern semi-conductor pigments, including those based on cadmium, chrome, and oxides of zinc, are brightly luminescent [24], but with a very short nanosecond decay kinetic [25] ascribable to interband transitions.

Hence, further analyses described in this paper have been carried out in order to suggest a possible identification for the white pigment used by Van Gogh.

4 Laboratory analysis of model paint samples

Laboratory analysis on the five commercial paint samples revealed that only two of them had a detectable luminescence emission (zinc white and Luminescent Green). Hence, in the following text only results pertaining these two samples will be described.

The emission properties of the zinc white sample (ZnO) are reported in Figs. 5a–5b. Its emission spectrum is characterized by an intense and narrow band peaked at 380 nm and two much broader bands with maxima at 430 and 520 nm, already reported by other authors [26]. The intense and narrow emission band at the shorter wavelengths is related to the near-band-edge excitonic recombination of the ZnO semiconductor [27], while the broad and weak emission in the green spectral region, known as the "trap state" emission, has been attributed to oxygen vacancies in the crystal [28].

Looking back at the emission registered on white areas of the Van Gogh painting (Fig. 2), it is evident that this unknown emission cannot be attributed to the presence of a zinc white pigment. No evidence of the intense band-gap of ZnO is observed which would be present in the emission spectrum as a marked shoulder at approximately 400 nm. For a complete characterization of the ZnO pigment, the emission decay kinetic was studied as well (Table 2): the band-gap emission at 380 nm is characterized by a very fast nanosecond decay with a main lifetime component close to 1.3 ns, whereas a slower decay characterizes the emission ascribed to oxygen vacancies in the crystal with a main lifetime component close to 4.1 μs.

The emission properties of Luminescent Green paint sample (ZnS:Cu) are reported in Figs. 5c–5d: the inorganic compound is characterized by a well-defined emission peak at 525 nm (FWHM = 100 nm) which resembles the spectral shape of the emission measured in the Van Gogh painting. The decay kinetic of Luminescent Green is a long-lived one with lifetime values of 60.4 μs (1.2%), 350.5 μs (30.8%), and 32.7 ms (68.1%).
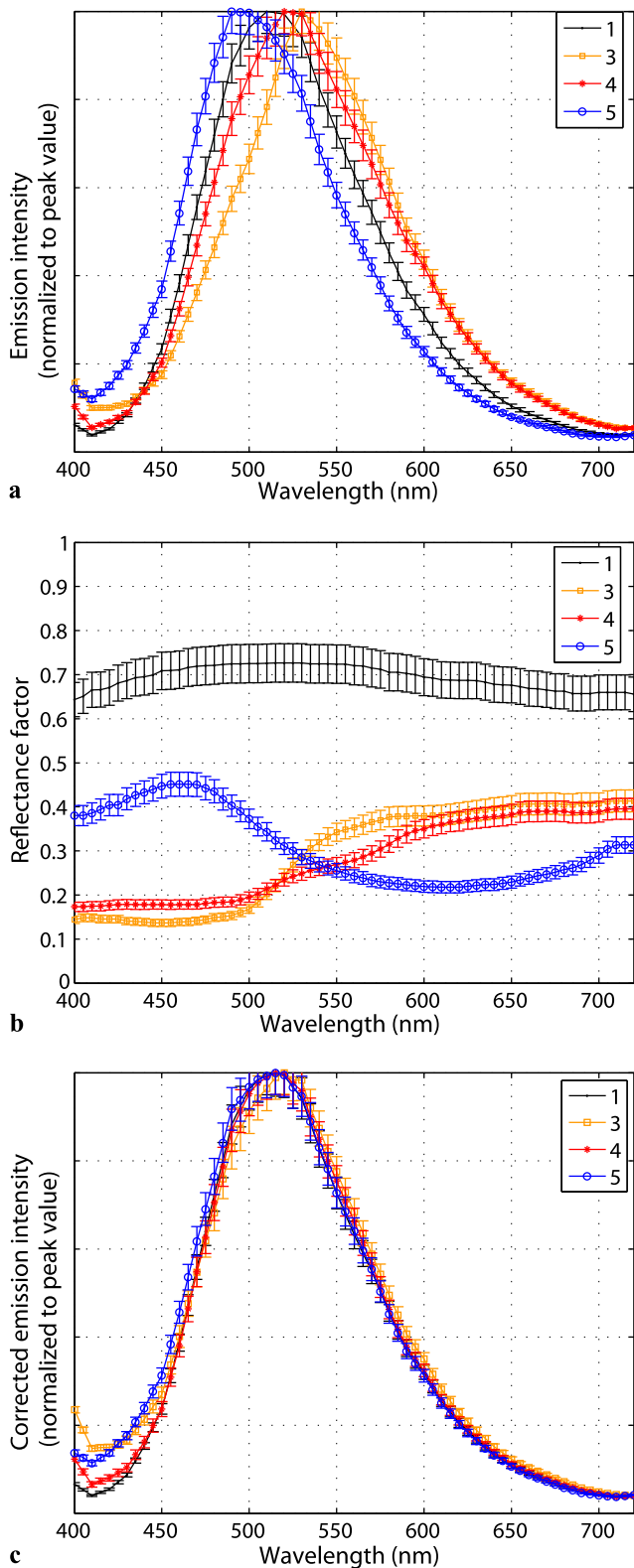
Fig. 4 (**a**) Emission and (**b**) diffuse reflectance spectra recorded from of areas 1, 3, 4, and 5 of the painting; (**c**) Emission spectra from the same areas corrected for selective absorption phenomena

5 Discussion

Luminescence properties of doped ZnS have been well known since the end of the 19th C. [29], when the material was first synthesized and used as a phosphor in many applications, from cathode ray tubes to X-ray screens to glow in the dark products [30–32]. The introduction of a few ppm of metal impurities (such as silver, copper, and manganese) in the crystal lattice gives rise to the formation of electron-hole recombination centers, inducing the formation of extra-energy levels from which radiative emission can occur. Activation with copper causes an emission mainly consisting of a green band (525 nm), assigned to monovalent copper ions incorporated into the host lattice by substitution in the zinc positions [31, 32]. A further blue band (460 nm) can be present (depending on the material preparation), attributed to associates between Cu ions occupying Zn^{2+} positions and interstitially incorporated Cu^+ ions. In terms of lifetime, the decay time of ZnS:Cu increases with copper concentration and can be further increased to several hours by adding small quantities of coactivators [31].

In summary, laboratory measurements let us ascribe ZnS:Cu as the possible inorganic crystal present in the long-lived luminescent areas of the Van Gogh painting. In particular, in terms of spectral properties, the emission from the Luminescent Green paint sample well resemble the one recorded in situ, whereas lifetime differences observed on the painting and on the model sample can be explained by a difference in copper concentration.

Since a pigment intentionally based on this doped inorganic semiconductor was not available during Van Gogh's lifetime, a possible hypothesis is that the Dutch artist employed a white pigment based on zinc sulphide (such as found in the pigment Lithopone) characterized by the presence of trace copper impurities nonintentionally introduced during pigment production. This hypothesis is supported by an in-depth study of the production process of Lithopone, of which a survey is synthetically reported below.

5.1 Historical context of Lithopone production

Lithopone is an intimate mixture of zinc sulphide and barium sulfate obtained through precipitation of a solution of barium sulphide and zinc sulfate [33]. It was first produced in 1874 according to a patent by J.B. Orr in England, followed by further patents in the next few years aimed at obtaining purer varieties [34]. Industrial production, established in the 1880s, continued vigorously until the early 1950s, benefiting from a substantial improvement introduced in the late 1920s which made the pigment lightfast by adding small quantities of cobalt salts prior to calcination [35]. Modern pure grade lithopone is not luminescent.

Fig. 5 Zinc White paint
sample: (**a**) full EES;
(**b**) emission spectrum following
excitation at 365 nm extracted
from EES; Luminescent Green
paint sample: (**c**) full EES;
(**d**) emission spectrum following
excitation at 365 nm extracted
from EES
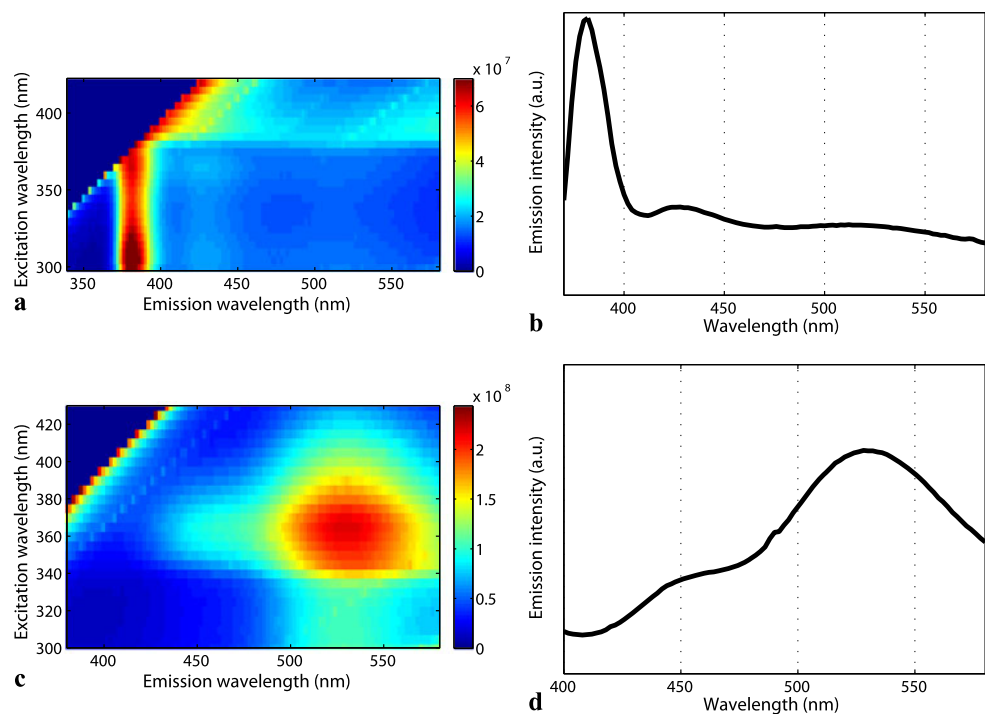
Table 2 Results of the nonlinear fitting procedure on emission decays measured from model paint samples by assuming a multiexponential decay model with a maximum of three components; lifetime values, $A\tau\%$ weights, and reduced chi-squared value are reported

Sample	Emission band	Gate width	τ_1	τ_2	τ_3	$A_1\tau_1$ (%)	$A_2\tau_2$ (%)	$A_3\tau_3$ (%)	χ^2
ZnO	370–390 nm	10 ns	1.3 ns	4.3 ns	–	96.5%	3.5%	–	0.0054
ZnO	400–700 nm	100 ns	200.1 ns	4.1 µs	26.7 µs	13.7%	59.5%	26.9%	0.0178
ZnS:Cu	400–700 nm	10 µs	60.4 µs	350.5 µs	32.7 ms	1.2%	30.8%	68.1%	0.0053

The presence of copper impurities in the synthesized pigment is largely dependent on the synthesis of its two constituting soluble salts, barium sulphide and zinc sulfate. In the decades close to Van Gogh's life, Lithopone production in Europe was confined predominantly to Germany, where barium sulphide was obtained starting from the Barite mineral, which is often very impure and contains salts of iron and other metals (and possibly also copper). The zinc sulfate solution was obtained starting from complex ores rich in zinc blende, which were roasted until the mineral was converted into zinc oxide, and subsequently treated with sulphuric acid to yield aqueous solutions of the metal ion [36]. Zinc ores can be highly impure, too, with typical impurities being lead, cadmium, iron and frequently copper, silver, gold, arsenic, and antimony. The purity of the zinc oxide produced starting from these ores is highly dependent on the roasting process employed, and it was only after 1916 that vertical retorts began to be used in Europe, when they replaced the horizontal ones, leading to a more efficient and pure smelting process [37]. Hence, it can be inferred that the zinc-based pigment produced in Europe before 1916 was much more impure than the one produced in more recent times, thus providing a possible explanation for inclusions which would lead to the microsecond green emission identified on the Van Gogh painting. Considering the above-mentioned roasting method, a further hypothesis is that the pigment used by Van Gogh is based on a ZnO pigment which contains copper-doped zinc sulphide impurities.

6 Conclusions

In situ measurements of a Van Gogh's watercolor revealed the presence of an unusual luminescent pigment, characterized by a distinctive microsecond decay kinetic. Laboratory measurements allowed us to suggest an assignment of this peculiar luminescence emission to a ZnS-based pigment characterized by the presence of copper impurities that were unintentionally introduced into the crystal lattice during the pigment production.

Further in situ measurements on the painting could eventually help in providing a confirmation of the proposed

identification, even though the discrimination among zinc-based modern pigments is not always straightforward with the aid of noninvasive analysis only, as was recently reported by the MOLAB laboratory during the investigation of the famous Mondrian's Victory Boogie-Woogie [38]. In the present case, portable reflectance spectroscopy in the UV [8] or Raman spectroscopy could eventually confirm the presence of zinc sulphide in the Van Gogh white pigment. However, the identification of copper in the pigment matrix is more complex due to the very low concentration of copper impurities in zinc sulphide, and the task could eventually be assessed by employing very sensitive XRF handheld devices.

Beside the possibility of further in situ measurements on the Van Gogh's painting, the present research paves the way for further detailed studies on modern pigments. It is in fact undoubtedly clear that different varieties of these inorganic materials have been synthesized during the 19th and 20th centuries. Hence, additional research and assessment of collections of historical paint tubes or of paint samples of modern paintings are still required in order to study their chemical composition and provide a better understanding of the production of these pigments during decades, as well as phenomena related to their degradation.

The role of luminescence spectroscopy techniques has been crucial during the present research. Whereas UV-induced luminescence (or fluorescence) photography is often considered as a rough qualitative diagnostic tool, the analysis of the luminescence emission from a work of art, when performed with proper well-designed and quantitative spectroscopy devices, may be extremely valuable. In particular, the analysis of the time-resolved decay of a luminescence emission in conservation science, available up to now in only few laboratories [16, 39], is of fundamental importance for studying both the common nanosecond emission from organic compounds and the slower microsecond and millisecond decay kinetic from luminescent inorganic pigments. We hope to be able to analyze other paintings by Van Gogh and by other modern painters with the same portable time-resolved camera in order to elucidate the possible occurrence of the same long-living luminescent pigment.

References

1. D. Bomford, J. Leighton, J. Kirby, A. Roy, *Impressionism: Art in the Making* (Yale University Press, London, 1990)
2. A. Katlan, J. Am. Inst. Conserv. **38**, 21 (1999)
3. G. Van der Snickt, J. Dik, M. Cotte, K. Janssens, J. Jaroszewicz, W. De Nolf, J. Groenewegen, L. Van der Loeff, Anal. Chem. **81**, 2600 (2009)
4. L. Monico, G. Van der Snickt, K. Janssens, W. De Nolf, C. Miliani, J. Verbeeck, H. Tian, H. Tan, J. Dik, M. Radepont, M. Cotte, Anal. Chem. **83**, 1214 (2011)
5. L. Monico, G. Van der Snickt, K. Janssens, W. De Nolf, C. Miliani, J. Verbeeck, J. Dik, M. Radepont, E. Hendriks, M. Gelodf, M. Cotte, Anal. Chem. **83**, 1224 (2011)
6. F. Casadio, S. Xie, S.C. Rukes, B. Myers, K.A. Gray, R. Warta, I. Fiedler, Anal. Bioanal. Chem. **399**, 2909 (2011)
7. J. Dik, K. Janssens, G. Van Der Snickt, L. van der Loeff, K. Rickers, M. Cotte, Anal. Chem. **80**, 6436 (2008)
8. M. Bacci, M. Picollo, G. Trumpy, M. Tsukada, D. Kunzelman, J. Am. Inst. Conserv. **46**, 27 (2007)
9. C. Miliani, F. Rosi, A. Burnstock, B.G. Brunetti, A. Sgamellotti, Appl. Phys. A **89**, 849 (2007)
10. F. Rosi, A. Burnstock, K.J. Van den Berg, C. Miliani, B. Brunetti, A. Sgamellotti: Spectrochim. Acta, Part A, Mol. Biomol. Spectrosc. **71**, 1655 (2009)
11. F. Rosi, C. Miliani, C. Clementi, K. Kahrim, F. Presciutti, M. Vagnini, V. Manuali, A. Daveri, L. Cartechini, B.G. Brunetti, A. Sgamellotti, Appl. Phys. A **100**, 613 (2010)
12. J.K. Delaney, E. Walmsley, B.H. Berrie, C.F. Fletcher, in *Scientific Examination of Art—Modern Techniques in Conservation and Analysis* (2005), p. 120
13. J.K. Delaney, J.G. Zeibel, M. Thoury, R. Littleton, M. Palmer, K.M. Morales, E.R. de la Rie, A. Hoenigswald, Appl. Spectrosc. **64**, 584 (2010)
14. F. Hocquet, H. Calvo del Castillo, A. Cervera Xicotencat, C. Bourgeois, C. Oger, A. Marchal, M. Clar, S. Rakkaa, E. Micha, D. Strivay, Anal. Bioanal. Chem. **399**, 3109 (2011)
15. http://www.vangoghletters.org/vg/. Letters 712, 823, and 827
16. D. Comelli, C. D'Andrea, G. Valentini, R. Cubeddu, C. Colombo, L. Toniolo, Appl. Opt. **43**, 2175 (2004)
17. D. Comelli, G. Valentini, A. Nevin, A. Farina, L. Toniolo, R. Cubeddu, Rev. Sci. Instrum. **79**, 086112 (2008)
18. D. Comelli, A. Nevin, G. Valentini, I. Osticioli, E.M. Castellucci, L. Toniolo, D. Gulotta, R. Cubeddu, J. Cult. Heritage **12**, 11 (2011)
19. G. Verri, C. Clementi, D. Comelli, S. Cather, F. Piqué, Appl. Spectrosc. **62**, 11 (2008)
20. L. Simonot, M. Thoury, J. Delaney, J. Opt. Soc. Am. A **28**, 1349 (2011)
21. D.V. O'Connor, D. Phillips, *Time-Correlated Single Photon Counting* (Academic Press, London, 1984)
22. B. Zitova, J. Flusser, Image Vis. Comput. **21**, 977 (2003)
23. B. Marino, Paints quantified Image analytical studies of preparatory grounds used by Van Gogh. Ph.D. thesis, University of Amsterdam (2006)
24. D. Anglos, M. Solomidou, I. Zergioti, V. Zafiropulos, T.G. Papazoglou, C. Fotakis, Appl. Spectrosc. **50**, 1331 (1996)
25. I. Borgia, R. Fantoni, C. Flamini, T.M.D. Palma, A.G. Guidoni, A. Mele, Appl. Surf. Sci. **127–129**, 95 (1998)
26. M. Thoury, J.P. Echard, M. Refregiers, B. Berrie, A. Nevin, F. Jamme, L. Bertrand, Anal. Chem. **83**, 1737 (2011)
27. J.P. Colinge, C.A. Colinge, *Physics of Semiconductor Devices* (Springer, New York, 2002)
28. K. Vanheusden, C.H. Seager, W.L. Warren, D.R. Tallant, J. Caruso, M.J. Hampden-Smith, T.T. Kodas, J. Lumin. **75**, 11 (1997)
29. E. Becquerel, C. R. Acad. Sci. **LXIII**, 188 (1866)
30. H.W. Leverenz, *An Introduction to Luminescence of Solids* (Wiley, New York, 1950)
31. G. Buxbaum, *Industrial Inorganic Pigments* (Wiley-VCH, Weinheim, 1993)
32. W.M. Yen, S. Shionoya, H. Yamamoto, *Phosphor Handbook* (CRC Press, Boca Raton, 2007)
33. W.J. O'Brien, J. Phys. Chem. **19**, 113 (1915)

34. C.L. Uebele, *Paint Making and Color Grinding* (The Trade Papers Publishing Co., 1913)
35. M. Van Alphen, *Paint Film Components* (National Environmental Health Forum, Adelaide, 1998)
36. The manufacture of lithopone: Ind. Eng. Chem. **4**, 775 (1912). doi:10.1021/ie50046a029
37. J.K. Almond, in *2000 Years of Zinc and Brass* (British museum, London, 1998), pp. 159–228
38. C. Miliani, K. Kahrim, B.G. Brunetti, A. Sgamellotti, A. Aldrovandi, M.R. van Bommel, K.J. van den Berg, H. Janssens, in *Proc. 15th Trienn. Conf. ICOM-CC*. New Dehli (2008), pp. 244–251
39. A. Romani, C. Clementi, C. Miliani, B.G. Brunetti, A. Sgamellotti, G. Favaro, Appl. Spectrosc. **62**, 1395 (2008)