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Executive Summary of the Thesis

An in-depth study of the photoluminescent properties of different variants of ultramarine blue pigment by time-resolved spectroscopy and micro-imaging

Laurea Magistrale in Physics Engineering - Ingegneria Fisica

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1. Overview of the Ultramarine Blue Pigment

Ultramarine blue is a blue pigment derived from lapis lazuli, a semi-precious stone that has been used as a decoration since the ancient Egyptians. This pigment entered European history from the port of Venice, in the 13th century, and immediately assumed great importance in medieval art due to its unparalleled and unusually stable bright color. Its geographical origin (probably the Badakshan region in present-day Afghanistan) and the laborious method of preparation meant that this pigment came at a price comparable to that of gold. Hence, it was a color that only appeared on the palettes of few renowned artists, and was dedicated to the most important figures in the religious iconography of the time: it could be found in the skies of religious scenes, or in the robes of Mary and Christ. The prohibitive price prompted artists to look for alternatives, so in 1828, the French Jean Baptiste Guimet discovered a method to produce artificial ultramarine blue at a tenth of the price of the natural one. His method is still used today.

In the field of art conservation, research on ultramarine blue revolves around three main questions: can we detect ultramarine blue on a painted surface? Is it possible to infer the geographical origin of the pigment without ruining the artifact under examination? And is it possible to distinguish the natural pigment (i.e. extracted in the traditional way) from the synthetic one?

2. The use of fluorescence spectroscopy and imaging in conservation science

In the field of art conservation and analysis, it is necessary to develop non-invasive techniques to examine artworks. As a result, the excitation of fluorescence has emerged as a non-destructive method to analyze painted surfaces and has been used by conservators and researchers alike since the 1920s, when UV lamps were invented.
Most pigments used from antiquity to relatively modern times have been inorganic compounds, either naturally occurring as colored minerals or carefully synthesized. Only a few of these inorganic pigments are luminescent when excited by

a proper excitation light. Further, often their luminescence is rather faint and in some cases related to the presence of impurities in the pigment formulation.
A critical limitation of the study of the emission spectra of pigments in paintings is that using a UV lamp as the excitation source and a steady-state spectrometer, it is impossible to separate the emission of inorganic pigments from the much more intense emission of the varnish or the binder. Therefore the resulting spectra are combinations of all.
To overcome this limitation, time-gated methods that use laser sources were developed. These methods use a pulsed laser source and a time-gated detector to distinguish luminescent materials based on their emission lifetimes, which, depending on the emitter and on the emission decay path, can vary from picoseconds to milliseconds. Luckily, organic materials, like organic pigments, varnishes and binding media have fluorescent lifetimes in the order of 1 to 10 ns, whereas inorganic pigments can be characterized by fluorescent lifetimes in the order of the microseconds [1]. A typical setup for these techniques consists of (1) a pulsed laser source, (2) suitable optics for the delivery of the laser radiation to the sample, (3) a system of lenses for the collection of emitted photons, (4) a time resolved detector (usually a time-gated intensified camera [2]) coupled with a spectrometer, a microscope or a camera lens. The time gated approach involves sending a laser pulse to the sample, which excites the fluorescent response, then waiting a set amount of time, depending on the specific decay kinetics of the sample, and finally opening a gate, allowing the emitted photons to be captured by the detector (either a spectrometer or a CCD camera). As shown in figure 1 the method allows the separation between the emission of nanosecond lifetime emitters (such as binders, colorants and varnishes) and that of micro- and millisecond lifetime emitters, which could be the defect-related emission ascribable to inorganic and semiconductor-based pigments and is typically at least one order of magnitude lower in intensity than the first one.

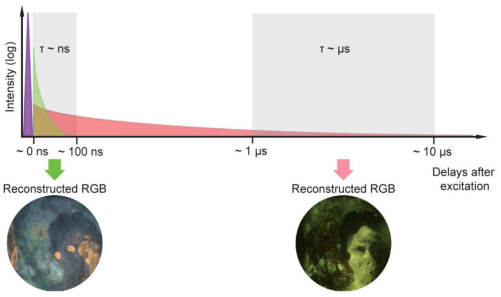


Figure 1: Example of time gated imaging. The two pictures are colorized according to the detected spectra. Notice how the fluorescent emission changes with time. Taken from [3].

3. Materials

Several variants of the ultramarine blue pigment have been analyzed. The samples are named "UB" followed by a number from 1 to 10. UB1 and UB2 are the lowest quality samples; UB3 through UB6 come from good quality Afghan lapis lazuli; UB7 and UB8 come from Chilean lapis lazuli; UB10 is the synthetic pigment.

4. Methods

In this section we will briefly describe the techniques employed in this thesis.

4.1. Optical Microscopy

A microscope equipped with multiple objectives (5X, 10X, 20X and 50X) and a color digital camera was used to observe the samples in dark-field and epifluorescence cofigurations. In the epifluroescence mode, optical emission of the samples was excited with the 365 nm line of a steady state mercury lamp. Although this test offered no quantitative information, it was useful to qualitatively characterize each sample.

4.2. Time-Resolved Photoluminescence (TRPL) Spectroscopy

Time-resolved photoluminescence (TRPL) analysis involves studying the evolution of the photoluminescence (PL) spectrum during the emission decay of the sample.
The measurement procedure involves detecting a sequence of PL gated spectra at different delays with respect to the laser pulses. Once a TRPL dataset has been collected, it is possible to extract time-gated PL spectra in selected temporal windows. In addition one can observe the emission decay of selected bands.

In this work three different TRPL datasets have been collected for each sample, related to the nanoseconds, microseconds and tens of microseconds emissions.

4.3. Fluorescence Lifetime Imaging (FLIM)

FLIM works by measuring the temporal properties of fluorescent emission at every point in a sample, which allows for the generation of a lifetime map of the analyzed region. This technique brings together the benefits of time-resolved spectroscopy and fluorescence imaging. The lifetime information effectively differentiates between various fluorophores, while the imaging capability of FLIM facilitates the localization of different fluorescent materials within the observed region. One of the limits of this technique is the fact that the emission lifetime is highly sensitive to the fluorophore micro-environment, so this parameter cannot be used for univocal material identification.
The fluorescence decay is sampled over time by repeated measurements with different delays between the excitation pulses and the leading edge of the gate, resulting in a sequence of fluorescence images captured at various time instants (as shown in figure 2).

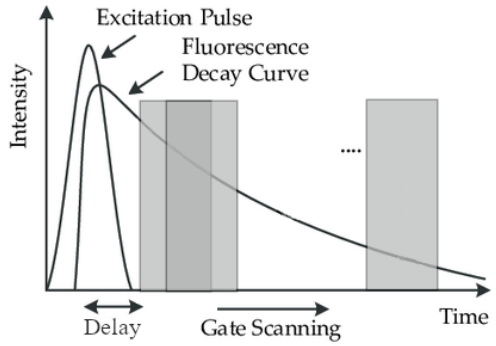


Figure 2: Representation of gate scanning method for the observation of the decay curve.

The result of the FLIM measurement are three maps of the sample:

- the intensity map, which displays the intensity of the fluorescence;
- the lifetime map, which is represents in false colors the mono-exponentially fitted lifetime of each pixel;
- the HSV map, which combines the previous two maps: the luminance of each pixel is correlated with the fluorescence amplitude, whereas the hue represents the lifetime of the pixel.

The lifetime map is calculated pixel-by-pixel by modelling the emission decays with a mono-exponential function and is then displayed as a map in a false color representation (as explained in [4]). Notably, in general luminescence cannot be modelled as a mono-exponential decay due to the multiplicity of relaxation paths (both radiative and non-radiative) a fluorescent species can undergo. Nevertheless, the reconstruction of the effective lifetime map based on a simple mono-exponential decay provides sufficient contrast to distinguish between different emitting species and is also independent from the intensity of the emission.

5. Time Gated Hyperspectral Imaging (TG-HSI)

Hyperspectral imaging consists of capturing images in numerous narrow and contiguous bands across the electromagnetic spectrum. Unlike traditional RGB (Red-Green-Blue) imaging, which captures only three color bands, hyperspectral imaging can capture hundreds or even thousands of bands, where each band basically corresponds to a specific wavelength of light, providing detailed spectral information about the examined object.
In this work, hyperspectral imaging has been employed together with photoluminescence measurements and the time gated approach to map different luminescent species on the basis of their different spectral and lifetime properties.
The resulting measurements are maps of the field of view (also referred to as "region of interest" or "ROI") colorized according to the measured spectra in each pixel. Averaged PL spectra can be extracted from selected pixels on the map, which in this case are constituted by single fluorescent particles. With the time gated approach, the maps of the spectra were recorded at three different delays with respect to the exciting pulse (0 ns, 1 µs and 10 µs), allowing us to observe the spectra of fluorescent particles at different time points.

6. Results

Here we present the results achieved with each of the employed techniques.

6.1. Optical Microscopy

All samples were observed with different magnifications and illuminated both with visible and UV light (365 nm line of a steady state mercury lamp). Below, as an example, we show the pictures of UB4 taken with 10X magnification.

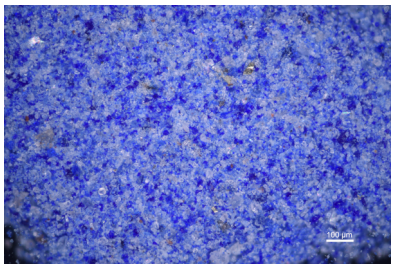


Figure 3: Pictures of UB4 taken with 10X zoom. Illuminated with visible light.

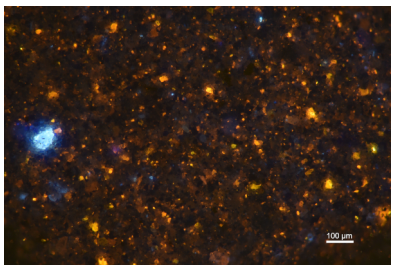


Figure 4: Pictures of UB4 taken with 10X zoom. Illuminated with UV light.

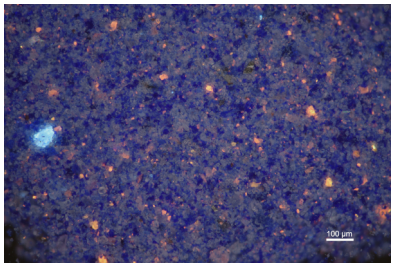


Figure 5: Combined UV and VIS pictures of UB4.

Through the analysis of the images from all samples, we observed that:

- among all samples, we have found blue-, yellow- and orange-fluorescent particles;
- the lower the quality of the pigment, the greater the density of blue-glowing particles.
- the higher the quality of the pigment, the greater the proportion of fluorescent particles of the yellow-orange kind.
- The fluorescence of the pigment doesn't come from the blue lazurite particles, that give lapis lazuli its color, but from the impurities found in the mineral, which under visible light appear as colorless particles. This consideration is confirmed by the fact that UB10, the artificial pigment, presents no fluorescence whatsoever since the impurities are not synthesized with the industrial method.

6.2. Time Resolved Photoluminescence (TRPL) spectroscopy

TRPL spectroscopy allow us to investigate the temporal evolution of the emission spectra. In figure 6 we show the TRPL dataset of UB2 as an illustrative example.

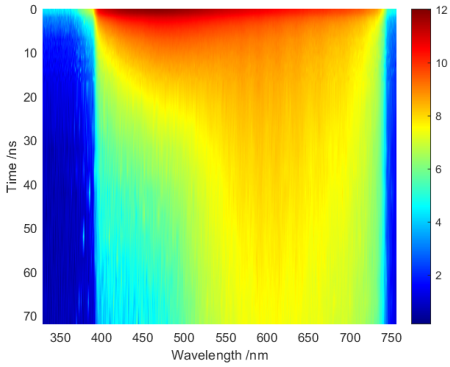
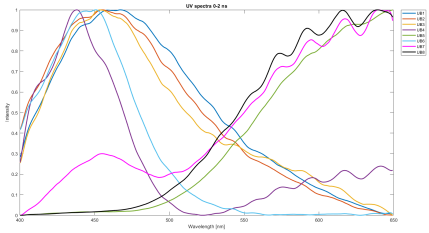
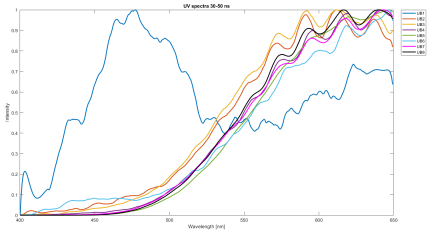


Figure 6: TRPL dataset of UB2. Gate: 10 ns; Delay range after excitation: 0-50 ns.

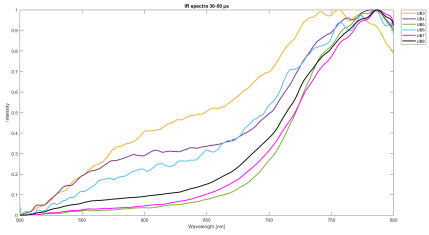
From figure 6 we notice that there there is a strong but short-lived band in the 430-460 nm interval (the "blue-band") and a weaker, but longer-lasting band in the 550-650 nm interval (the yellow-orange band, "y/o-band"). In other samples (UB3 through UB8), at longer delays still a further band has been detected in the 720-800 nm interval (the infrared band, "IR-band").



(a) 0-2 ns. Spectral interval: 400-750 nm.



(b) 30-50 ns. Spectral interval: 400-750 nm.



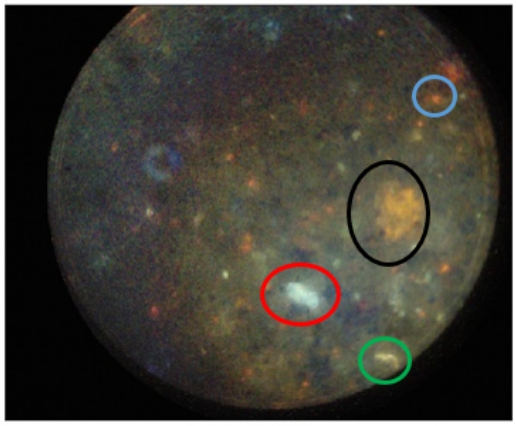
(c) 30-50 µs. Spectral interval: 500-800 nm.

Figure 7: Gated spectra.

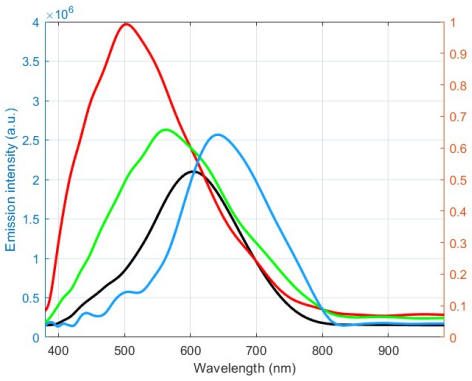
We have found that the blue-band has a lifetime in the order of few nanoseconds; the y/o-band in the order of the microseconds; the IR-band in the order of the tens of microseconds. In figures 7a, 7b and 7c, one can see how as time goes on, the fluorescence emission shifts towards longer wavelengths.

6.3. Time Resolved Methods: TG-HSI and FLIM

TG-HSI and FLIM measurements taken at the nanoseconds, microseconds and tens of microseconds timescales confirm what has been found with TRPL. Below we show a TG-HSI picture of the nanoseconds emission of UB2, colorized according to the measured spectra, and the spectra of selected particles.



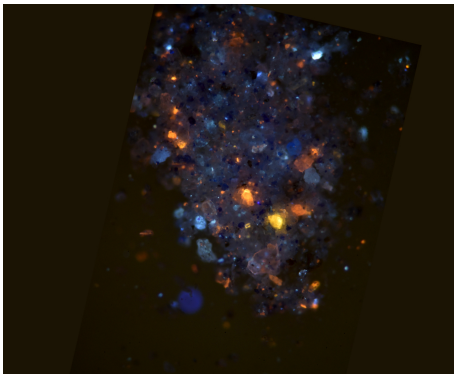
(a)



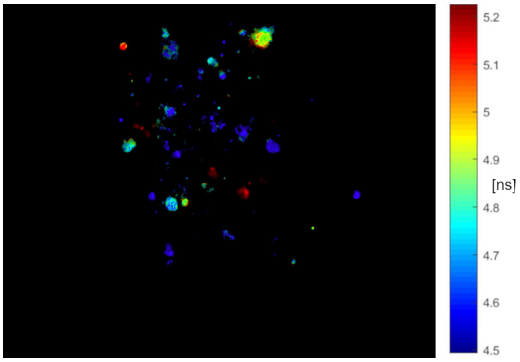
(b)

Figure 8: TG-HSI measurement of UB2 at nanoseconds timescale. a) ROI of UB2 colorized according to the measured spectra. Gate: 10 ns; Delay after excitation: 0 ns. b) Spectra of the circled particles in the corresponding color.

Figure 8 shows that particles of the blue-fluorescent kind are the strongest emitters right after excitation (see the particle circled in red). Yellow-orange emitting particles do fluoresce at this timescale, but their emission is weaker and lasts much longer.
The FLIM measurement correctly separates emitters with radically different lifetimes, which in our case are the blue fluorescent particles and the yellow or orange fluorescent particles. Below we show a UV picture of UB2 and the HSV map of the ROI at the nanoseconds timescale.



(a)



(b)

Figure 9: FLIM measurement of UB2. a) ROI of UB2, picture taken at 15X magnification with UV light illumination. b) HSV picture of the ROI.

Notice how in the HSV map (figure 9b) its mainly the blue-fluorescent particles that appear. This is because at this timescale their emission is generally much stronger than that of the yellow-orange emitting particles. Some particles of the latter kind can still be seen and appear as dim red dots in HSV map, signifying that their emission is weaker, but longer-lasting.

7. Conclusions and Future Developments

Thanks to the application of time-resolved photoluminescence based techniques we have managed to characterize the fluorescent emission of different variants of ultramarine blue pigments. We have found that the source of the fluorescence of this pigment is not to be attributed to the blue lazurite particles, which are responsible for its color, but instead to some of the naturally occurring impurities in lapis lazuli, which appear as colorless particles when observed with a microscope. This has immediately allowed us to achieve one of the objectives of this work: distinguishing between natural pigments, which fluoresce, and artificial pigments, which do not. We have characterized multiple kinds of fluorescent impurities depending on their emission spectra and lifetimes. In particular we have found:

- blue-fluorescent impurities, which feature an emission band in the 430-460 nm spectral range and which present the lowest lifetime in the order of few nanoseconds;
- the yellow-orange impurities, which emit in the 550-650 nm range and have lifetimes in the order of the microseconds. In some cases we have managed to separate the yellow-fluorescent impurities from the orange-fluorescent impurities thanks to differences in lifetimes;
- infrared-fluorescent impurities (only in higher quality samples), which emit in the 720-800 nm range and are characterized by the longest lifetime, in the order of tens of microseconds.

We have also observed that the higher the quality of the pigment, the stronger the yellow-orange and IR component of fluorescence.
We have not managed to link specific fluorescent features to the geographical origin of the lapis lazuli from which the pigment is extracted. More samples from Chilean and Siberian sources should be characterized before attempting to answer the provenance question. Judging by the results of this work, it is reasonable to assume that with time resolved PL alone we would be capable of distinguishing between higher quality pigments and lesser quality ones, by the density of blue fluorescent impurities. The next step would be to pair PL techniques with non-invasive molecular analysis methods, like Raman spectroscopy, to identify the fluorescent impurities, which up to now have only been called by the color of their fluorescence spectrum, and see if they can be linked somehow to the provenance of the sample.
Finally, the results of this work indeed show that there is fertile ground for the employment of time resolved PL techniques for the study of ultramarine blue pigments in paintings.

References

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