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Laser spectroscopy methods for an 18th century grisaille painting investigation

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This paper presents a study regarding the quality of particular painting techniques - grisaille, black and white colors on thick paper, in case of an about 200 years old artwork, using exclusively two analytical laser techniques: Laser Induced Fluorescence (LIF) and Laser Induced Breakdown Spectroscopy (LIBS). The investigation aimed the identification of the type of white and black colors, and an other possible specific color (yellow or ochre) compounds (which were not allowed by this technique). The results proved again the known efficiency of each mentioned investigation technique, but also the conclusions that could be drawn from the correlated experimental data. The fast and efficient experiment took advantage of : i) double pulse LIBS technique that allows a more intense signal to be acquired,a reduced material consumption, the elimination of the matrix effect; ii) fast data mapping and characterization of critical points all over the painting using LIF scanning image.

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1. Introduction

Two laser analytical techniques, Laser Induced Fluorescence (LIF) and Laser Induced Breakdown Spectroscopy (LIBS), have been applied on the painting named *Landscape,* by an unknown author of Flemish school of the 18th century.

The painting is executed in a special technique: grisaille - black and white colors on carton — a technique used in gray tint monochrome paintings, which permitted to obtain some effects on painting's details. The photographic equivalent would be a Sepia Tone.

Working in grisaille was often chosen because it was a quicker and cheaper technique, although the effect was sometimes deliberately chosen for aesthetic reasons. Grisaille paintings resemble the drawings, normally in monochrome, that the artists from the Renaissance on were trained to produce. Some consider that they can also betray the hand of a less talented assistant more easily than a fully colored painting. However, suggestive shadows and details were difficult to obtain with less "instruments", and the quality of these works, were obviously strongly related with craftsmen's virtuosity.

The picture in discussion, dated between 1780 and 1820, belongs to a private collection and its investigation was requested by the Art Collection Gallery. This paper does not present a common study regarding the materials used, to establish the artwork's restoration history, authenticity or conservation status – like many other papers reported [1-3] – but present a study of the quality of the mentioned painting technique. As it was specified, only two sorts of pigments must be found in the case of an "honest" author. Because of the artwork age and of the improper storage in the past, some slight yellowish areas are noticed. The main question from specialists is about their origin. The supposed origins are: a possible third color or a natural ageing of the applied colors or of the support – paper – or a dirt deposition.

Fig. 1 Landscape with marked LIF and LIBS interrogated points

The artwork protection and minimal intervention during the analysis are mandatory and have lead to laser spectroscopy methods usage, being validated as accurate and non-invasive methods (in LIF cases) or as accurate but micro-invasive methods (in case of LIBS), and also fast and without sample preparation. The simplicity of the technique permits in-situ characterization or simple screening. The possibility to use the technique in-situ eliminates the need for sampling, a process, which is time consuming and in some cases inflicts physical damage to the artwork's surface. This is important because the sensitivity and value of most works of art objects often precludes sampling thus preventing the use of analytical techniques, such as the atomic absorption spectrometry (AAS) or inductively coupled plasma - mass spectrometry (ICP-MS), which require a small quantity of sample that is consumed during the measurement. Obviously, non-destructive techniques are preferred over destructive ones and even though LIBS is not strictly a non-destructive technique it is considered minimally invasive given the very small area of interaction of the laser pulse with the sample surface. On the basis of these features and research done to date, LIBS appears as a useful alternative to other sophisticated techniques, for obtaining information on the elemental composition of materials in cultural heritage objects. The potential of LIBS in this field is shown by several research papers that have appeared in the last few years, describing its use for the analysis of works of art and objects of archaeological importance [4,5]. Earlier reports can also be found on the use of laser micro-spectral analysis in the determination of the elemental content of metal, pottery and paint samples from different objects [6,7]. The analytical capabilities of LIBS are dealt with in more detail in the following sections and in the examples presented.

The problem of pigment's LIBS analysis in the case of paintings consists in a low laser energy permitted and a thin layer of pigment. Because of these aspects, resulting LIBS signal is very low. Beside this, LIBS signal of different layers of dirt could induce a difficulty in the chemical elements identification. Special attentions have to be spent for elements like Pb, Fe, Mn that are often present in dirt layers' composition and in paints composition, too.

With other words, the investigation will search by LIF and LIBS the type of the white and black colors, and implicit the specific compounds of possible yellow or ochre colors.

2. Experimental

2.1 Methodology and experimental setup

It is expected a Pb origin identification by comparative LIF and LIBS signals, extracted for several critical points all over the picture, and with various white/black ratio. In case that there are correlations between LIF and LIBS signals, it means that the Pb's origin is the constituent color. Obviously, if there are no correlations, the Pb's origin is the dirt layer.

Due to the well-known advantages of the LIBS by double pulse laser technique that allow a more intense signal and a less material consuming, there were made some analyses using methods. More than that, it is known that this method eliminates the matrix effect. [8]

The experimental arrangement for the optical irradiation path has one laser beam perpendicular on the surface and the other one parallel with that surface – another solution for less material consumption.

The LIBS investigation on the observable and disturbing yellowish areas will prove no "fraudulent" existence of the third color if elements like Fe and Fe oxides – from yellow or ochre colors – will be determined. By contrary, a LIBS signal without Fe indicates that the painting's yellow tint origin is more likely to be related to natural causes, not to .

For LIBS experiments were used two lasers: Tempest 300 (New Research) @355nm and Giant G 70 10 (Quanta System) @1064 nm with maximum energy at 20 mJ and 350 mJ, respectively.

The Tempest laser system was used for irradiation of surface and Giant, with delay of pulse at 4 ms respective Tempest, passed parallel with paint's surface

The detection system was composed with Spectrograph Mechelle (Andor) and ICCD-DHK734 Gen III (Andor).

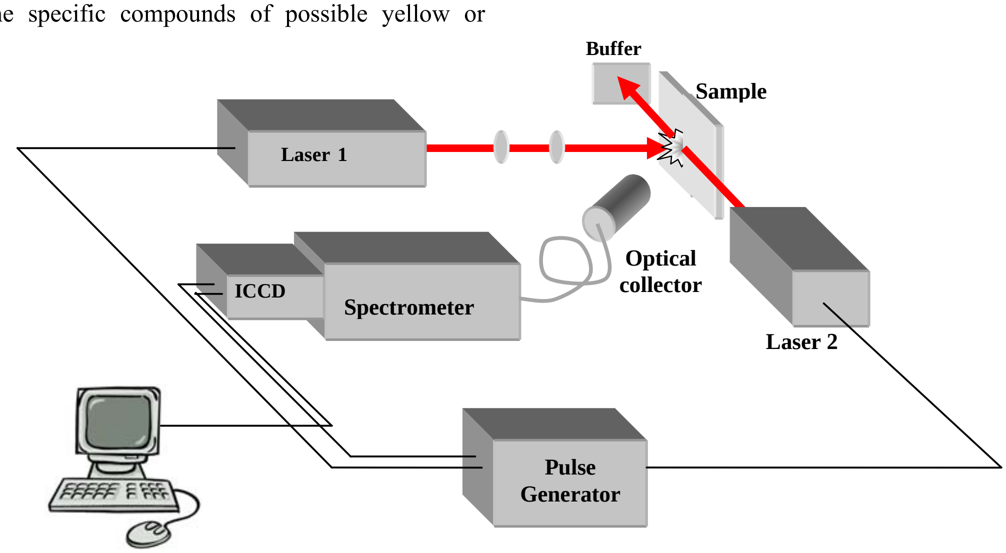


Fig. 2 Double pulse LIBS system.

Detection delay was 2 µs and the width was 12 µs. Impulse generator model 9518 (Quantum composers) synchronized the two lasers and the ICCD sensor.

The **LIF system** is a scanning device based on a coaxial system of irradiation and detection. For the irradiation it has been used a FQSS 266-Q@266nm laser,with 1.25 µJ per pulse, 3 kHz, pulse duration 1 ns (Crylas) and a QE65000 spectrometer (Ocean Optics).

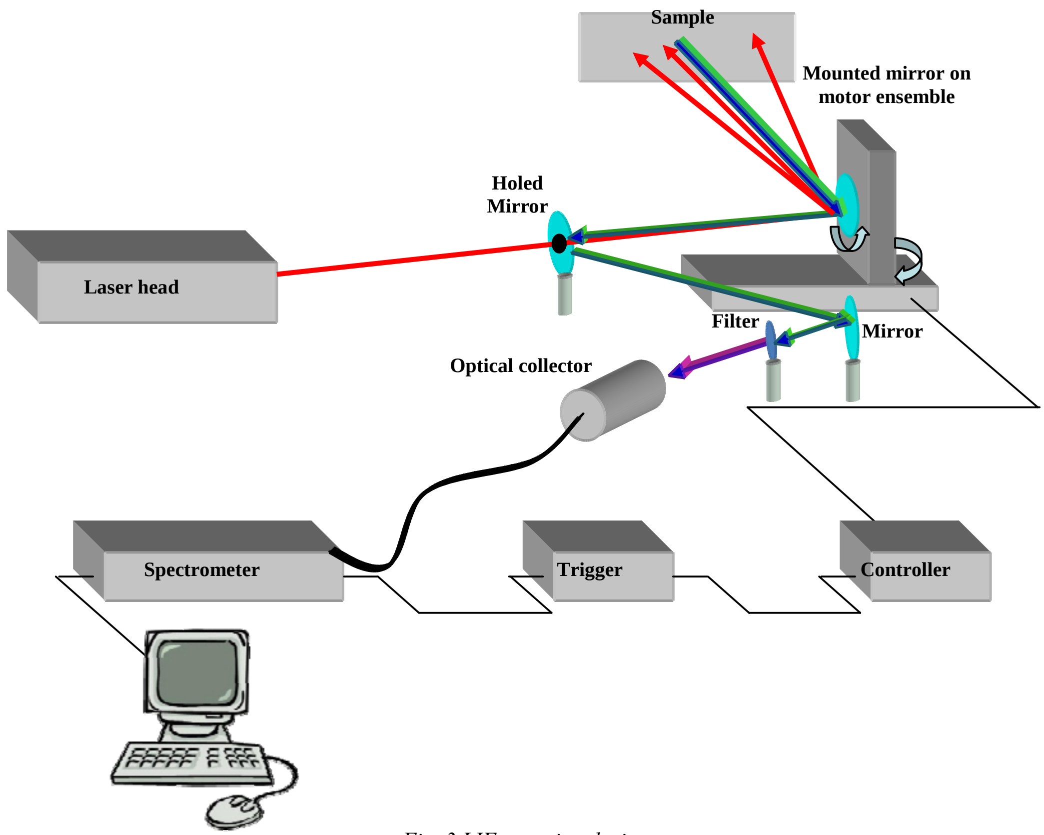


Fig. 3 LIF scanning device

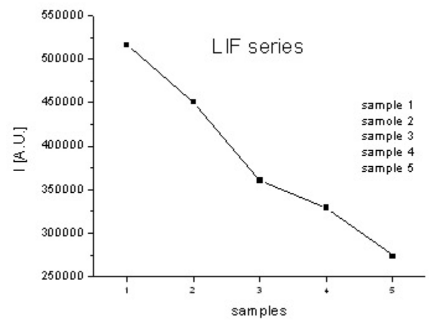
3. Results and discussion

3.1 Preliminary experiments

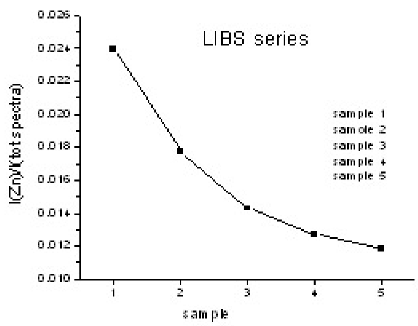
Before the micro-destructive experiment on the painting, an investigation was performed on samples realised with various grey tones, as mixture of two pigments: Ivory black [$Ca_3(PO_4)_2$+C+$MgSO_4$] and white based on the Zn. LIF signal was determined only for white pigment, having no LIF signal from black paint.

For the LIBS signal we have taken the ratio between the intensity of Zn peaks and the integral over entire detected spectrum.

Five different tones between white and black were used. But only in the case of double laser pulses - presented in this paper - correlation between LIF and LIBS intensities were obtained. (Fig.4)



a



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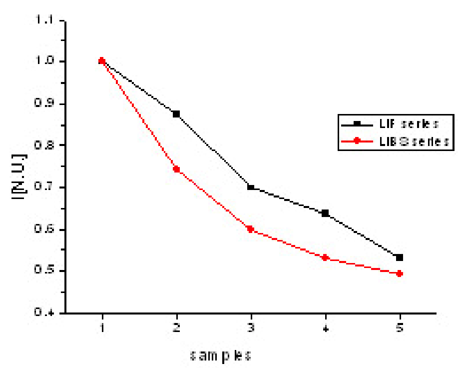

c

Fig. 4a LIF series of the selected samples with 5 different white and black mixtures (white→black) b. LIBS series of the selected samples with 5 different white and black mixtures (white→black), c Normalized spectra of the selected samples with 5 different white and black

3.2 The investigation of the painting and discussions

Using the LIF scanning technique it has been obtained the characteristic peaks mapping of the black and white paints knowing that the intensity of the characteristic fluorescence peaks are depending on the paint's concentrations.

The efficiency of the proposed invention method was demonstrated by the significant information from LIF scanning image (Fig.5b) compared with the information extracted from ordinary picture (Fig.5a). For example, the white color concentration on two points (7 & 8) is more visible by contrast on LIF scanning image than on ordinary picture.

Fig. 5a Photo image, b Bands 500 nm & 520 nm.

Relevant results by LIF scanning have been obtained by overlapping the collected data at 500 nm and 520 nm (*Fig. 5b*).

Fig.6 shows all LIF spectra for the 8 selected and interrogated points and - as it was presumed – all of them are ordered like the intensity of these points with more or less white color.

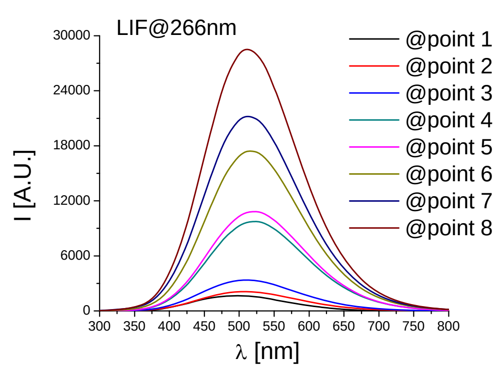

Fig. 6 Peak intensities of the LIF spectra (of the 8 points on the painting) increases as white/black pigment ratio increases.

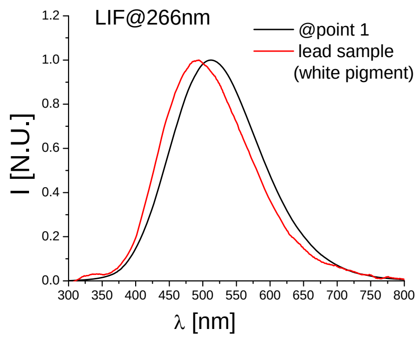

Fig 7 Comparation of a normalised spectrum of a lead sample and of an interrogated point on the painting

All LIF punctual investigations results (fig.6,7) suggest that the white color is made based on Pb pigment. Also, LIBS punctual investigation results (see Table 1) confirm the Pb presence.

Coming back to the original supposition about the Pb origin identification, pigment or dirt layer, the correlation has been studied.

Table 1

Interrogated point	Detail	Detected spectral line λ[Å]	Integral spectra I_{tot} [A.U.]	I_{Pb}/I_{tot}
1	Black area under rock	3639.57; 3739.94; 168.03	185096	1.04E-03
2	Dark grey bush	3639.57; 3683.46; 739.94; 4057.81; 5201.44	224818	1.19E-03
3	Light grey bush	2823.19; 2873.31; 3572.73; 3683.46; 3739.94; 4057.81; 4062.14; 5201.44; 6001.86	155124	1.44E-03
4	Yellowish grey area	3683.46; 3671.49; 3739.94; 4057.81; 4062.14; 6001.86	91338	1.37E-03
5	Yellowish with area	2873.31;3683.46; 4057.81; 6001.86	102584	2.10E-03
6	With snow	2823.19; 3683.46; 3671.49; 3739.94; 4057.81; 5201.44;	87889	3.00E-03
7	Cow's back	2801.99; 2823.19; 2833.05; 3572.73; 3671.49; 3683.46; 3739.94; 4019.63; 4168.03; 5201.44	182736	4.20E-03
8	With spot on cow	2801.99; 2833.05; 3572.73; 3639.57	137087	6.17E-03

It could be observed that in the analyzed points of the painting, the LIBS signals of Pb increases (Fig. 8b). When the black pigment fraction in the mixture decreases, the LIF signals increases too (Fig.8a). Normalized comparative diagrams of LIBS and LIF signals of the 8 selected points proved the correlation between these two types of signals (Fig.8c). In conclusion the with pigment is based on the Pb.

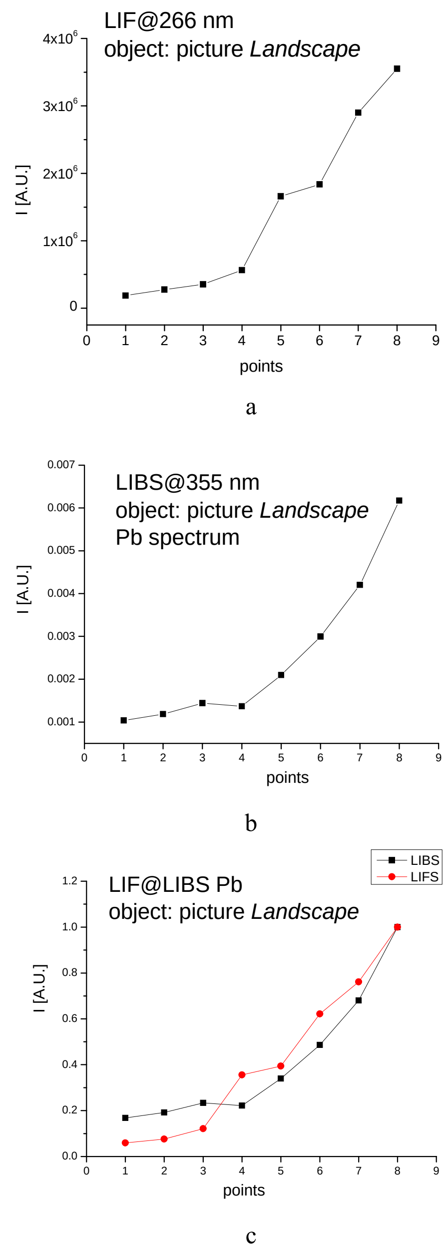

Fig. 8. a LIF signals of light and dark points (dark → light), b. LIBS signals of light and dark points (dark → light), c Normalised comparative diagrams of LIBS and LIF signals of light and dark points (dark → light).

Due to the traditional self made colors receipt that mandatory included Ca element in white Pb based colors as redox element, and was no surprise when a significant part of the LIBS spectra included Ca signals. For this reason, a part of research was focused on the presence of Ca, too.

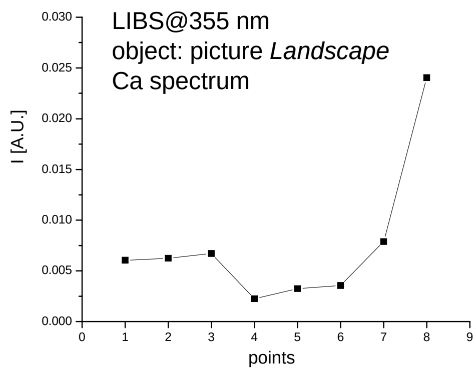

Fig. 9 Ca presence in all studied points

Unexpected at the first glance, the presence of Ca in darker points (1,2,3) is more evident than in lighter ones (4,5,6). Evidently, Ca presence in lighter points (4…8) comes from its contribution to white as redox agent, and its presence in darker points could be explained by the origin of black color based on black ivory pigment.

The very low peak intensities of Fe in all of the 8 interrogated points – including the one with the yellowish tint (5) – does not sustain the supposition of the existing of a third color based on yellow or ochre pigment. In addition, LIF spectra in the same points (Fig. 8a) show a small deviation in respect with the Point 5 response increasing, which is a normal as long as the nature of the surface was slightly changed. The slight modification responds with a little higher intensity of LIF signal, but with no specific elements that could come from a third color.

4. Conclusions

The combination of the LIBS and LIF techniques sustained each other and generated complementary results about the painting surface composition.

LIF scanning has been successfully used for the selection of the interesting LIBS points (case of only 7 points –fig.1), therefore reducing the invasive effect on the surface.

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