ANALYTICAL STUDIES OF POLYCHROMES BY TIME-INTEGRATED LASER-INDUCED BREAKDOWN SPECTROSCOPY

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Time integrated Laser Induced Breakdown Spectroscopy was applied to the study of real samples of polychromes. Two samples respectively from the Spanish Baroque and from the XV century were analysed. The time integrated spectra showed negligible contribution of continuum background emission. The spectra of the Baroque sample indicated the presence of vermilion; this was confirmed by Near Infrared Fourier Transform Spectroscopy. LIBS spectra of the XV century sample showed Ca, Al, Mg, Na and Pb lines and the molecular emissions CN(B-X) and C_2(d-a). Relative spectral intensities were measured as a function of the number of laser pulses delivered on the same position of the sample. The LIBS analysis was compared to an exhaustive analytical study.

Keywords: Laser induced breakdown spectroscopy; lasers in art conservation; excimer laser ablation

1. INTRODUCTION

LIBS (Laser Induced Breakdown Spectroscopy) has proved to be a powerful technique to obtain information about the chemical composition of the surface and underlying layers of a diversity of materials [1]. In recent years the technique has been applied in artwork conservation [2] providing information to characterise contaminants of marbles and

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stone [3, 4] and to help to identify pigments and binding media in painted artworks [5]. Model samples have been the subject of most studies and comparatively less effort has involved the much more complex real systems. In this work we have carried out LIBS of real samples of polychromes that have been collected for analytical purposes from monuments under restoration; in some of these, previous and exhaustive information, collected by a variety of analytical techniques, is available. Comparison between the different results can help to establish valid correlations relating the elemental analysis provided by LIBS to the complex materials involved in real samples.

LIBS relies on the detection of the ablation plume produced in the laser interaction with the sample. For a diversity of materials and laser excitation sources, it has been observed that light from the ablation plume emission typically lasts for less than 10 µs after the ablation event [6–8]; time resolved LIBS experiments have shown that during the first hundred ns, the atomic emission lines are superimposed on a strong background continuum, which results in a poor signal-to-noise ratio and hinders the detection of weak features [1, 9]; broadening of the spectral lines by the Stark effect has also been observed to take place at short times, decreasing remarkably after the first microsecond [10]. For this reason LIBS is more commonly used with time resolution, requiring the use of expensive gated detectors with enhanced sensitivity. In this work LIBS analysis has been carried out with time-integrated detection using an inexpensive CCD camera system and the results have been compared with those obtained for the same sample by the time-resolved detection mode.

2. EXPERIMENTAL TECHNIQUES

The output of an excimer laser (XeCl at 308 nm, pulses of 10 ns), directed normally to the sample, is focussed by a 10 cm focal length lens. A plastic fiber optic cable of 1 mm diameter is positioned at an angle near 45° with respect to the irradiated surface and separated from the surface 1–4 mm. The optical fiber collects the emission produced in the ablation plume originating in the interaction of the laser with the sample. The light emerging form the opposite end of the optical fiber is dispersed by a 0.25 m spectrograph (CVI corporation,

DKSP-240), coupled to a CCD camera (SBIG, ST-6V). The spectrograph has an effective aperture ratio of $f/3.9$ and reciprocal linear dispersion of 3.2 nm/mm and is provided with gratings (1200 l/mm) to cover the spectral range 180 – 1500 nm. The CCD camera spectral response is in the range 200 – 1100 nm; the detector array dimensions are 8.6×6.5 mm and the number of pixels is 750×30 in the resolution mode used in this work. For a given wavelength setting in the spectrograph, the recorded spectral range is about 25 nm.

An external trigger signal provided by a delay generator (SRSDG535) ensures that the arriving of the laser pulse takes place during the integration time of the CCD camera; the exposure time in the CCD camera is set to the minimum value or 0.01 s.

The typical spectral range covered in the present work is 350 – 700 nm and therefore several laser shots are needed to record the whole spectrum. Even at moderate laser fluences, in some materials, a few laser shots can suffice to produce ablation of a complete layer; therefore in order to analyse, over the whole spectrum the same layer of the sample, the latter was mounted on a translation stage, allowing fine displacement along a plane perpendicular to the laser beam.

3. DESCRIPTION OF SAMPLES

Sample 1 is a gilded altar piece of Baroque style from the church of Santiago in Montilla (Córdoba, Spain). The analysis has been performed on a red coloured area of the unvarnished surface.

Sample 2 is a varnished polychrome of the XV century, on a wooden substrate. Several layers of binding media and polychrome material can be observed.

4. RESULTS AND DISCUSSION

4.1. Comparison Between Time Resolved and Time Integrated LIBS Spectra in Sample 1

The spectra of Sample 1 obtained upon irradiation with a XeCl laser (17 mJ), detected by the CCD camera system is shown in Figure 1. The spectrum is compared to that obtained after irradiation of the same
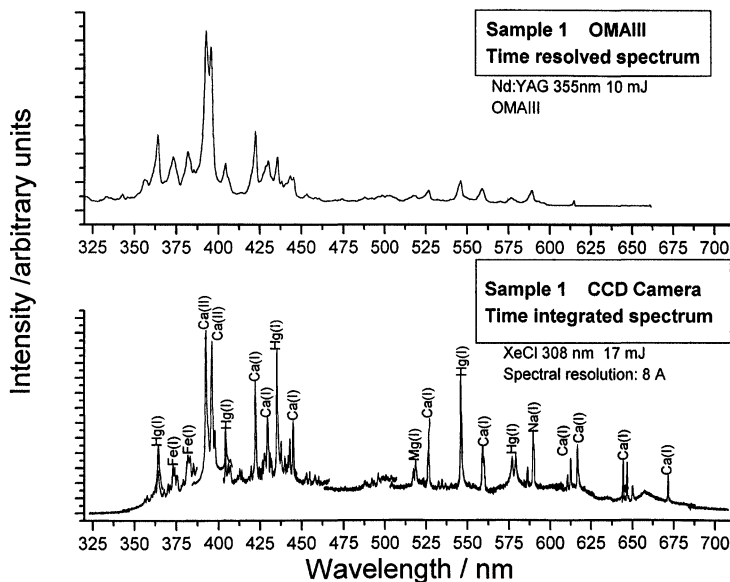
FIGURE 1   LIBS spectra of Sample 1. Time resolved spectrum (delay 500 ns; gate 500 ns) and time integrated spectrum (exposure time 0.01 s).

sample with the third harmonic of a Nd : YAG laser at 355 nm (10 mJ) and similar focussing conditions, using a 0.25 m spectrograph and intensified diode array Optical Multichannel Analyzer OMA detector. For the latter, the emission is collected with a temporal window of 500 ns delayed 500 ns from the laser pulse; a single laser shot suffices to record the whole spectrum, that is shown in Figure 1. Despite the differences in resolution both spectra show a close similarity. The most prominent features around 395 nm consist of partially overlapped lines of Ca and Al. Other Ca emissions, several Hg lines and Na are also present in the spectrum Studies carried out in model samples [5] have shown that Hg lines are indications of the pigment vermilion HgS. The presence of HgS was further assessed by the use of Near Infrared Fourier Transform Raman spectroscopy [11, 12]; the latter was performed with a RFS 100/S-G Bruker spectrometer equipped with a microscope accessory. The sample was excited at powers below 100 mW by a Nd : YAG laser at 1064 nm and the scattered radiation from a surface of a few square microns was collected in backscattering (or 180°) geometry.

The rest of the LIBS spectra is dominated by Ca emission lines that can also be associated to calcium derivatives commonly added to increase the volume of the vermilion pigment [5].

4.2. LIBS Analysis of Sample 2

The LIBS spectra obtained upon irradiation of brown pigmented area of Sample 2 was recorded. It has been shown [5] that information about the composition of the different layers can be obtained by examining the changes in the LIBS spectrum with the number of laser pulses impinging on the same position of the sample. In the present work several LIBS spectra were recorded, each one after a given number of delivered laser shots. The results are depicted in Figure 2. Most of the intense features appearing in the different spectra can be assigned. Several lines can be assigned to Ca, Al, Mg and Na. Within the limited spectral resolution, the relatively intense line near 405 nm could be assigned either to Hg or Pb; however the absence of any other Hg emissions, particularly the strong lines near 436 and 546 nm, that are prominent features in the spectrum of Sample 1, clearly support the second assignment to the Pb line at 405.8 nm. The broad structured features peaking at 387 nm, 474 and 516 nm are readily assigned to the molecular $CN(B-X, \Delta v = 0)$ and to the $C_2(d-a, \Delta v = 1$ and $\Delta v = 0)$ Swan bands. The broad features around 550 nm and 620 nm are in the same spectral regions as the band sequences $\Delta v = -1$ and $\Delta v = -2$ of the Swan system, but this assignment can be disregarded according to the spectral analysis of the successive layers of the sample discussed below.

In the following, the spectra obtained after successive laser pulses on the same position of the sample will be briefly described. C_2 molecular emissions are absent from the spectrum obtained with a single laser shot, appear very distinctively after the second, and decrease slowly in intensity for higher numbers of laser pulses. The opposite behaviour is observed for the doublet emission near 526 nm corresponding to neutral atomic Ca; for this, irradiation with a single laser pulse gives rise to an strong emission that decreases sharply as ablation of the surface proceeds with successive laser shots. A similar behaviour is observed for the weaker Mg doublet emission near 518 nm. This is illustrated in Figure 3. The molecular emission $CN(B-X, \Delta v = 0)$,
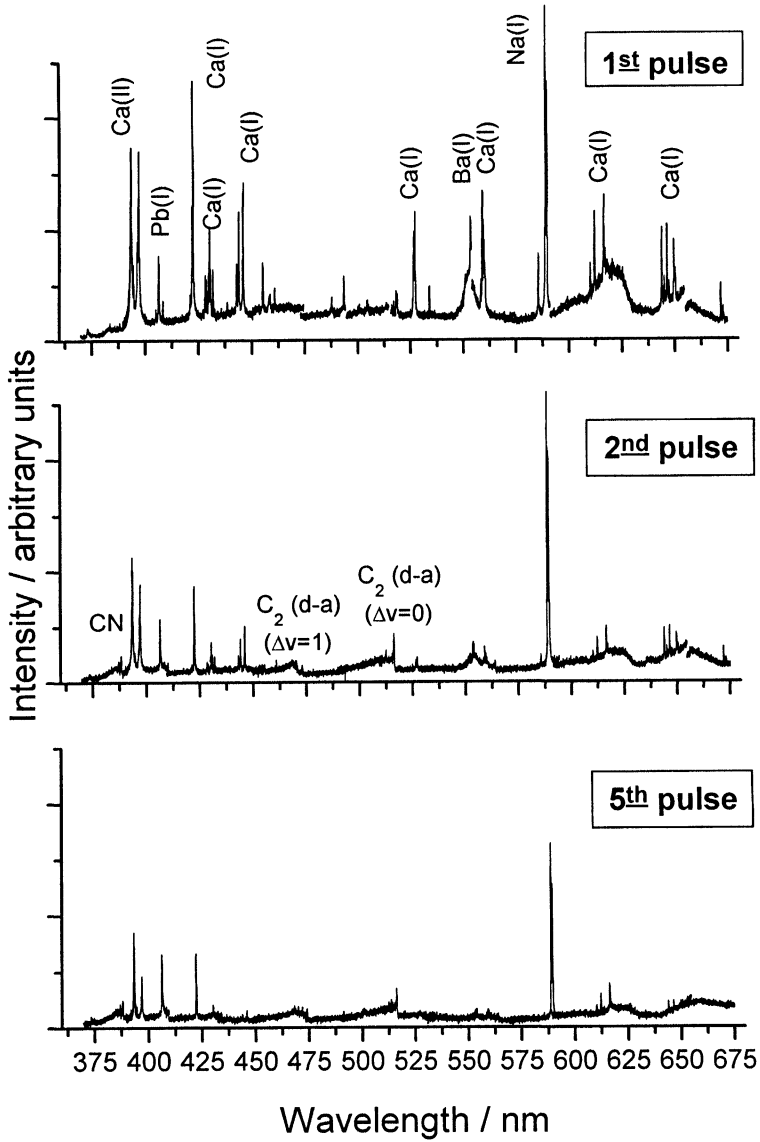
FIGURE 2   LIBS spectra of Sample 2. Spectra obtained after successive laser pulses delivered on the same point of the sample. Spectral resolution is 0.32 nm.
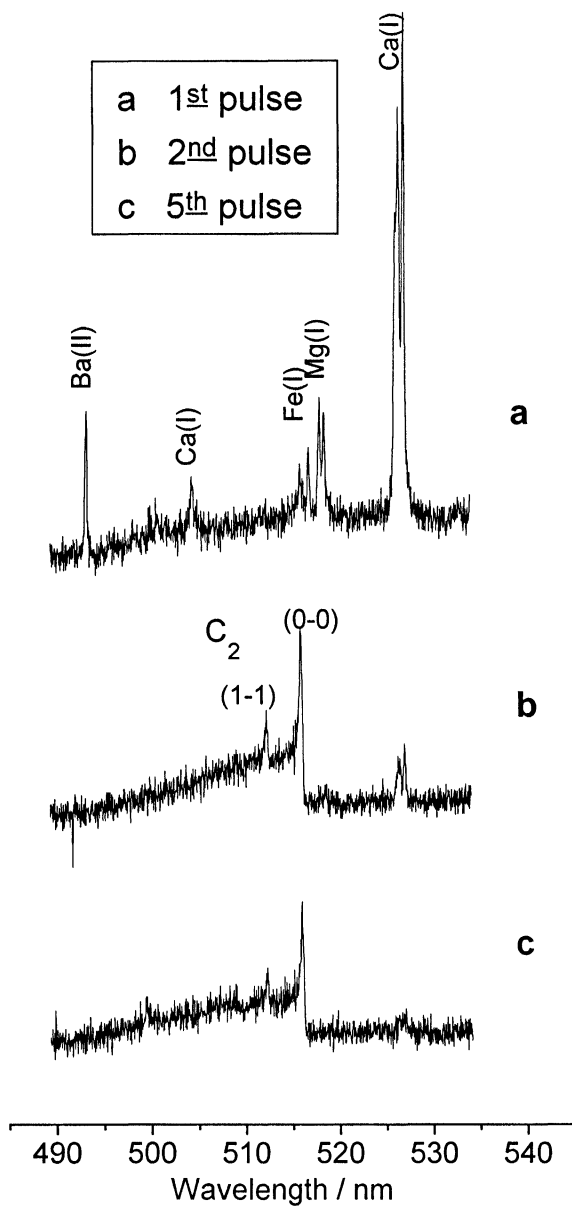
FIGURE 3   LIBS spectra of Sample 2. C_2(d-a, $\Delta v = 0$) molecular emission obtained by ablation of Sample 2 after successive number of laser pulses. Spectral resolution is 0.32 nm.

overlapped by other weak lines, and the unassigned broad features around 550 nm and 620 nm are observed since the first laser shot; the CN bands appear more prominently after the second pulse. The neutral atomic Al lines overlapping the strong ionic Ca emissions near 395 nm have only appreciable intensity in the single shot spectrum. The rest of the observed emissions decreases monotonically with increasing number of laser shots except that assigned to Pb that remains roughly constant. The Na doublet near 589 nm is the most prominent emission in all spectra obtained after the first and successive laser shots.

In the following, the simple elemental analysis described above can be compared with an exhaustive analysis carried out with a variety of techniques over more than 100 samples found at the same location as "Sample 2". According to this analysis the original polychrome is protected in many areas by a natural varnish. In some areas, the natural varnish appears covered by overpaintings; the latter have been applied over a layer of gypsum, that lies on the original polychrome, or over an organic layer also isolating the original work. The overpaintings contain several pigments; the most commonly found in the different samples analysed are lead white, indigo and modern pigments as lithopone and synthetic ultramarine blue. The underlying layers, belonging to the original polychrome, contain several organic and inorganic pigments; lead white and red lead (minimum) are the most abundant pigments; they have been found either as the single component of a layer or mixed with other coloured pigments as ivory black, orpiment, vermilion and the organic pigments indigo and alizarin. The paint layers have been applied on a wooden substrate covered by a gypsum layer and previously isolated with an organic binding media.

The chemical composition of the above materials together with a summary of the results obtained by the LIBS analysis is given in Table I. The observation of Pb obtained in the LIBS analysis in all ablated layers is consistent with the presence of the pigments lead white and red lead, found in several layers and in a large number of the samples analysed by conventional analysis. Ca lines have been found to have a variety of sources; a pollutant layer of calcium carbonate is generally present on the surface and is removed with the first ablated layers. In the sample analysed in this work, the behaviour of the neutral atomic

TABLE I   Chemical composition of the different layers of Sample 2 and atomic and molecular emissions identified by LIBS

Layer	Pigment	Formula [12]	LIBS Emission
External contaminated layer		$CaCO_3$	Ca
Overpaintings	Lead White	$Pb_3(CO_3)(OH)_2/PbSO_4 \cdot PbO$	Pb
	Indigo	$C_{16}H_{10}N_2O_2$	
	Lithopone	$ZnS + BaSO_4$	
	Ultram. blue (synt)	$Na_{6-10}Al_6Si_6O_{24}S_{2-4}$	Na, Al
	Clay	Different compositions	
			Mg
Gypsum/ Organic Layer/ Nat. Varnish		$CaSO_4 \cdot 2H_2O$	Ca
		Polymers of 2methyl-1,3 butadiene	C_2
Pigments (Original Polychrome)	Red lead	Pb_3O_4	Pb
	Lead White		Pb
	Ivory Black	$Ca_3(PO_4)_2 + C + MgSO_4$	Ca
	Orpiment	As_2S_3	
	Vermilion	HgS	
	Indigo		
	Alizarine	$C_{14}H_8O_4$	
Gypsum layer		$CaSO_4 \cdot 2H_2O$	Ca

Ca emission at 526 nm, rather intense after ablation with the first laser shot and nearly disappearing in successive spectra, differs from the slowly decreasing behaviour of other Ca (ionic) lines; this suggests that the former could be related to pollutants on the surface or to the outermost overpainting layers. It has been pointed out that the spectra obtained in the laser removal of overpaintings are dominated by the emission lines of the metal constituent of the accumulated salts or of the pigments employed [13]. Al and Na lines that in the LIBS analysis appear to be associated with the external layers might also be related to the pigment ultramarine blue (synthetic) and clays present in the overpainting composition. Molecular emissions CN(B-X) and C_2(d-a) have been found in the ablation of several polymers [8, 14]; in relation to painted artworks the molecular emissions are usually attributed to ablation of the polymeric material that constitutes the natural resins used in varnishes. It was mentioned above that for the samples studied in this work the original varnish appears in many cases covered by overpaintings; this would be consistent with the behaviour of the C_2

emissions observed in this work, absent in the spectrum of the first ablated layer; other components, such as the organic binder of the pigments [5], might also give rise to the molecular emissions observed. Finally the Na emission obtained in all successive ablated layers cannot be related to any of the pigments identified in the analysis of the original polychrome and its source remains to be investigated.

5. CONCLUSIONS

Real samples of polychromes have been studied by LIBS. Spectra recorded respectively collecting the time integrated and time resolved emission provided entirely similar information. Atomic lines and molecular band emissions could be observed with negligible contribution from a background continuum.

Despite the inherent inhomogeneous character of the real samples, the simple LIBS analysis of successive ablated layers, performed in a small volume of the sample, was able to provide information about themost abundant pigments present in the polychrome. However, changes in relative intensities of the molecular emissions as laser ablation penetrates the sample, did not suffice to establish a valid correlation between the organic material (binding media and varnishes) and the molecular emissions observed in the ablation plume. Research in progress in our laboratory, on the same real samples studied here, applying LIBS time resolved techniques, indicate a markedly different temporal behaviour for the different emissions in the ablation plume; the measured temporal profiles are also dependent on the distance to the surface, roughly resembling the behaviour observed in polymer ablation studies [15]. More work in this direction is planned in order to get a better understanding of the ablation process in complex real systems.

References

[1] Cremers, D. A. (1987). *Appl. Spectrosc.*, **41**, 572.
[2] Fotakis, C., Anglos, D., Balas, C., Georgiou, S., Vainos, N. A., Zergioti, I. and Zafiropulos, V. (1997). *OSA TOPS on Lasers and Optics for Manufacturing*, **9**, 99.
[3] Maravelaki, P., Zafiropulos, V., Kilikoglou, V., Kalaitzaki, M. and Fotakis, C. (1997). *Spectroch., Acta B*, **52**, 41.
[4] Gobernado-Mitre, I., Prieto, A. C., Zafiropulos, V., Spetsidou, Y. and Fotakis, C. (1997). *Appl. Spectrosc.*, **8**, 1125.
[5] Anglos, D., Couris, S. and Fotakis, C. (1997). *Appl. Spectrosc.*, **51**, 1025.
[6] Sappey, A. D. and Nogar, N. S. (1994). In: *Laser Ablation, Principles and Applications*, Miller, J. C. (Ed.), *Springer Series in Materials Science*, **28**, 157.
[7] Hermann, J., Boulmer-Leborgne, C. and Dubreuil, B. (1990). *Appl. Surf. Science*, **46**, 315.
[8] Srinivasan, R. and Braren, B. (1989). *Chem. Rev.*, **89**, 1303.
[9] Bescos, B., Castaño, J. and González Ureña, A. (1995). *Laser Chem.*, **16**, 75.
[10] Aguilera, J. A., Aragon, C. and Campos, J. (1992). *Appl. Spectrosc.*, **46**, 1382.
[11] Best, S., Clark, R., Daniels, M. and Withnall, R. (1993). *Chem. Brit.*, **29**, 118.
[12] Clark, R. J. H. (1995). *Chem. Soc. Rev.*, p. 187.
[13] Georgiou, S., Zafiropulos, V., Anglos, D., Balas, C., Tornari, V. and Fotakis, C. (1998). *Appl. Surf. Science*, **127−129**, 738.
[14] Tsuboi, Y., Sakashita, S., Hatanaka, K., Fukumura, H. and Masuhara, H. (1996). *Laser Chem.*, **16**, 167.
[15] Davis, G. M., Gower, M. C., Fotakis, C., Efthimiopoulos, T. and Argyarakis (1985). *Appl. Phys. A*, **36**, 27.