Hindawi Publishing Corporation
Laser Chemistry
Volume 2006, Article ID 42709, 5 pages
doi:10.1155/2006/42709

Research Article

Laser Cleaning and Spectroscopy: A Synergistic Approach in the Conservation of a Modern Painting

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Received 15 September 2006; Revised 17 November 2006; Accepted 17 November 2006

Recommended by Marta Castillejo

We present results from preliminary laser cleaning studies performed on a 20th century modern painting, in which laser-induced breakdown spectroscopy (LIBS) was employed for monitoring the progress of material removal. This synergistic approach, that combines laser ablation cleaning with spectroscopic control, is of obvious importance as it offers a reliable means of ensuring proper conservation and could be the basis of a standard protocol for laser-based restoration procedures.

1. INTRODUCTION

Laser cleaning methods have been employed over the past three decades in a number of conservation cases including the removal of surface deposits and/or contamination, corrosion layers, materials from previous conservation treatments and overpaint layers from different types of cultural heritage objects [1–4]. The effectiveness of modern laser cleaning methodologies has been gaining recognition and lasers have been successfully used in quite a few cases of encrustation removal from archaeological and historical stone sculpture and monuments [3–5]. On the other hand, laser cleaning of painted artworks has been demonstrated [3, 4, 6] but its application remains mostly at the research level because materials in paintings are quite diverse and often complex and sensitive, requiring delicate and highly controlled procedures. Currently, research is in progress for understanding the interaction of laser radiation with such complicated structures and the mechanism behind material removal in order to achieve proper conservation.

In all cases of restoration, reliable monitoring tools are necessary that will enable control of the cleaning. Simple means such as the naked eye of an experienced conservator provide control as cleaning is performed but with limited capabilities. On the other hand, more sophisticated analytical tools are available, including different types of microscopy and spectroscopy, but these are used off-line or require sampling. Laser induced breakdown spectroscopy (LIBS) has been proposed and used as a diagnostic tool for monitoring and controlling the laser cleaning process [7–10]. One of the most interesting features of LIBS is its ability to perform depth profile analysis. Revealing the sratigraphy of a painted structure, namely, finding the successive paint layers, is obviously quite important in the characterization of a painting regarding the technique used or the presence of overpaintings or retouching. In the case of laser cleaning, LIBS can be performed in situ by using pulses from the same laser and this way, one is able to monitor the progress of material removal on-line by recording the corresponding spectra [6–9].

Conservation problems in modern paintings are quite diverse and include, for example, degradation of complex materials, for which one often has limited knowledge, or previous unsuccessful restoration treatments. Furthermore, in certain cases the original materials and those to be removed are quite similar and thus setting discrimination boundaries between them is extremely difficult if not impossible. These cases pose a challenging and highly demanding conservation problem and a laser restoration approach might turn out to be useful. Some practical and technological issues in the development of a proper laser cleaning protocol for works of contemporary art are discussed, with respect to the use of on-line depth profiling of the painting.

2. EXPERIMENT

In this paper, we discuss a set of preliminary laser cleaning tests performed at IESL-FORTH, on a 20th century modern painting from the Guggenheim Museum of New York. The painting was part of Ad Reinhardt's "Black Square" series (1966). It had travelled extensively until the early 1980s, suffered various damages, and was completely over-painted with an acrylic emulsion and a transparent "sealant." Removal of these overpaint layers was not possible with standard conservation methods [10, 11] and therefore a collaboration between IESL-FORTH and the Guggenheim Museum was set up to investigate the possibility of laser cleaning. The aim of the work was to establish proper laser cleaning parameters that would give rise to controlled removal of the overpaint layers. More specifically this work presents results from the investigation of the possibility of using LIBS as a monitoring tool during the laser cleaning of modern materials. In principle, on the basis of the characteristic LIB spectra recorded, one may be able to discriminate among different overpaint layers as these are progressively removed. In cases in which the plume emission produced during laser ablation might not be intense enough to yield a clean LIB spectrum, an alternative approach is followed. Single pulses with proper fluence (higher than that used for cleaning) from the same laser are delivered in between successive cleaning scans to probe a small area on the exposed surface. This way, an incremental depth profiling is performed parallel to cleaning that enables one to follow the progress of material removal. The latter approach has been used in this study.

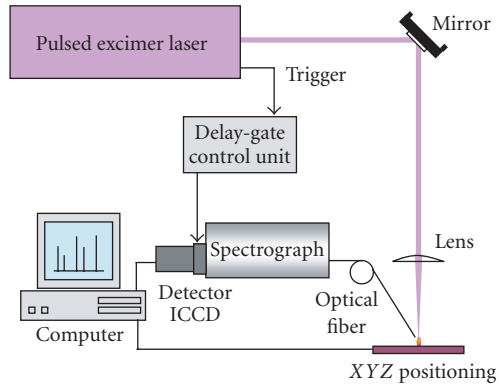

Figure 1: Schematic diagram of experimental setup for laser cleaning and LIBS analysis.

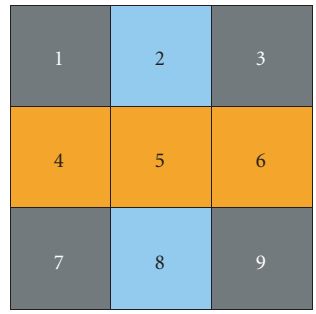

Figure 2: Schematic representation of the colored layers of the overpainting.

3. MATERIAL AND METHODS

A diagram of the experimental set up used for laser cleaning and LIBS analysis of the painting is presented in Figure 1. The painting was mounted on a motorized xyz-stage, controlled by a computer. The stage enabled positioning of the painting close to the focal plane of the laser beam (z-axis) and allowed its precise lateral translation (xy-plane) with respect to the laser beam. A KrF excimer laser emitting at 248 nm (COMPex Lambda Physik, pulse duration: 30 nanoseconds) has been employed for both the cleaning application and the LIBS measurements.

The laser beam is focused on the painted surface by means of a cylindrical planoconvex quartz lens ($f = +300$ mm) that results in illumination of a $3.7 \times 0.4\,\text{cm}^2$ rectangle on the painting surface. The beam is scanned in the direction perpendicular to the long dimension of the focused rectangle, across a preselected area that is typically 1–3 cm long. A set of 5–10 pulses are applied at each individual rectangle. To obtain a homogeneous surface exposure, successive rectangles are overlapped to a degree of 80%. Typical laser fluence for laser cleaning was about $1.1\,\text{J/cm}^2$ while for the LIBS analysis, performed in between successive cleaning scans, the fluence was increased at approximately $2\,\text{J/cm}^2$ by adjusting the focussing lens. The light emitted from the plasma plume was collected with an UV transmitting optical fiber oriented roughly at the center of the illuminated rectangle at an angle of 30° with respect to the normal to the painting surface. The plasma emission was analyzed in a 0.20 m spectrograph (PTI model 01-001AD) equipped with two diffraction gratings of 300 and 1200 grooves/mm and the spectrum was recorded on an intensified CCD detector (Andor Technologies, DH520-18F-01). The plasma emission was recorded with a delay of 500 nanoseconds with respect to the laser pulse with an integration window of 500–1000 nanoseconds.

4. RESULTS AND DISCUSSIONS

Following preliminary tests on replicas (model samples), cleaning trials were carried out on selected areas of the painting. The painting is a $1.55 \times 1.55\,\text{m}^2$ square subdivided to 9 equal squares in a 3×3 arrangement with subtle variations of black. The overpaint structure consisted of symmetrically grouped pigment layer patterns, following the geometry of the original painting (Figure 2).

Analysis of selected cross sections from all 9 squares, by using SEM-EDS and optical and FT-IR microspectrometry, provide some insight into the stratigraphy of the overpaint layers, which is very valuable as a reference for the LIBS results and especially important for the interpretation of monitoring and cleaning results. Cross sections showed that squares 1, 3, 7, and 9 had blue and red paint layers,

Table 1: Indicative stratigraphy obtained from cross-section analysis of squares 2 and 6.

Square 2		Square 6	
Layer*	Components	Layer*	Components
18 17 16 15 14	Acrylic emulsion with low pigment concentration	20 19 18 17 16 15	Acrylic emulsion with low pigment concentration
13	Black paint (black iron oxide, bone black)	14	Black with red paint (red cadmium sulfoselenide, black or red iron oxide)
12	Blue paint (cobalt oxide)	13	Black paint (black iron oxide, bone black)
11	Black paint (black iron oxide, bone black)	12	Black with red paint (red cadmium sulfoselenide, black or red iron oxide, barytes)
10	Blue paint (cobalt oxide)	11	Yellow paint (black iron oxide, bone black, chromium yellow)
9	*Acrylic sealant layer*	10	*Acrylic sealant layer*
8 7	Paint mixture of black and blue (black iron oxide ultramarine blue)	9 8 7 6	Paint mixture of black and blue (black iron oxide, ultramarine blue, barytes)
6 5 4 3 2	Paint mixture of black, blue, and green (black iron oxide, ultramarine blue, chromium green, barytes)	5 4 3 2	Paint mixture of black and blue (black iron oxide, bone black, ultramarine blue, cerulean blue, barytes)
1	Ground layer (titanium dioxide)	1	Ground layer (titanium dioxide)

*Layer numbering starts from the ground layer with the outer layers receiving the highest number.

squares 2 and 8 had blue, and finally squares 4, 5, and 6 had red and yellow paint layers under the final black overpaint. The stratigraphy of squares 2 and 6 that have been examined in detail in this study is given in Table 1.

Single pulse LIB spectra were collected following a certain number of laser cleaning scans over the preselected area. For example, representative spectra obtained during cleaning over square 2, are shown in Figure 3. The spectrum obtained before starting the cleaning, corresponds to material rich in acrylic medium and this is demonstrated by the emission bands of C_2 (excited carbon dimers) at around 476 nm and 512 nm and also by the fact that the emission from neutral Ca (422.67 nm) is stronger than the one arising form Ca ions (393.37 and 396.85 nm). The latter indicates a lower plasma temperature expected for the pigment poor outer acrylic layer that is not strongly absorbing at 248 nm. Following the first cleaning scan (10 pulses), the LIB spectrum indicates the presence of Ca, Fe, Co, Al, Cu, and Na, suggesting that material has been removed down to layers 13/12 or 11/10, which combine black and blue pigments based on iron and cobalt respectively (see Table 1). In addition, the spectrum suggests the presence of a Cu based pigment, which could either be azurite (blue) or malachite (green). It is noted that optical microscopic examination of the cross section sample shows green pigment grains dispersed in the black layers 13 and 11. The strong Ca emission arises most likely from the pigment bone black, $Ca_3(PO_4)_2$. Following 3 cleaning scans with 5 pulses each, we reach a new layer that shows different pigment composition rich in Fe, Al, Ba, Ca, and Na. Emission from Ba indicates the presence of barytes (white pigment or filler based on $BaSO_4$), while the increase of Al and Na emission correlates with the presence of the blue pigment ultramarine blue, $Na_8Al_6Si_6O_{24}S_3$. Most likely these spectra correspond to layers that are just below the acrylic sealant, on the top part of the original paint and signal that cleaning should end before that level.

In square 6, several spectra were also collected during the progress of cleaning that reveal the presence of different layers (Figure 4). Following scan 1, material containing Fe, Ca, and Al is seen, that most likely corresponds to the top layers of the light black acrylic overpaint (20–15). Following scan 3, new emissions show up from Ba, Mn, and Cd besides those from Ca, Al, and Fe. The emission due to Cd correlates with the presence of cadmium red (see Table 1) and suggests that layers 14/13/12 have been reached. The presence of Mn might indicate the use of manganese brown or black. Most

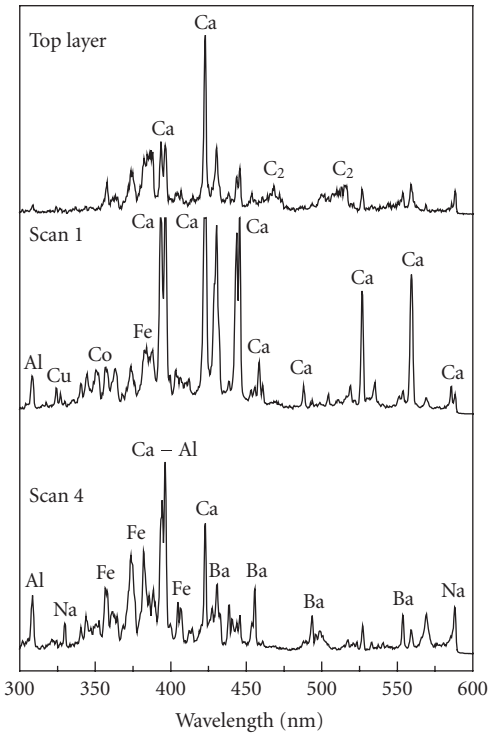

Figure 3: LIBS monitoring of the laser cleaning process at square 2.

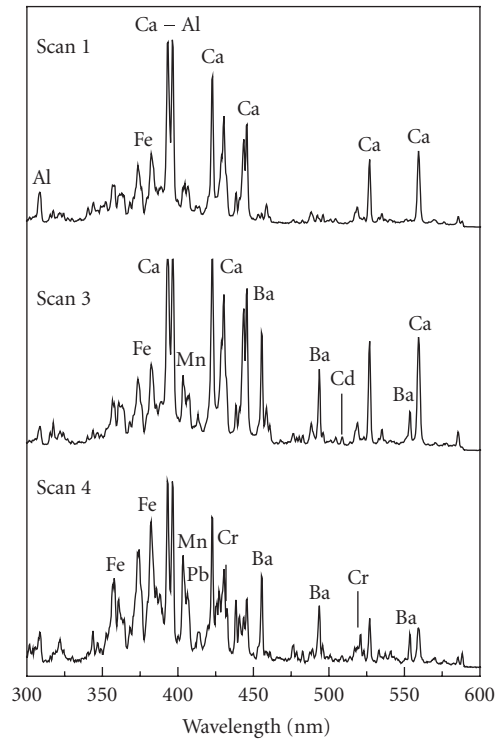

Figure 4: LIBS monitoring of the laser cleaning process at square 6.

importantly, following scan 4, two new emissions from Cr and Pb are observed, which suggest the presence of chrome yellow, $PbCrO_4$, one of the components in layer 11. This is just over the sealant that has been applied on the original paint and therefore determines the cleaning limit.

These results indicate that LIBS offers a potential tool for monitoring laser cleaning of multi-layer paint structures and in certain cases it can be used to signal the end-point of cleaning protecting the original paint. The presence of mixtures of pigments with several components results in rather line-rich spectra and both high resolution and broad spectral coverage are highly desirable. The use of echelle type spectrometers should be promising for such demanding applications of LIBS [12]. Finally, one has to note that an optimum approach to such complex conservation problems is to follow a specific procedure, that includes first detailed analysis and understanding of the materials present followed by controlled conservation innervation. On the basis of these preliminary results, a more extended laser conservation campaign for the painting has been undertaken at Art Innovation (the Netherlands) and results will be reported in the future.

ACKNOWLEDGMENTS

This work has been supported by the Ultraviolet Laser Facility operating at IESL-FORTH and by AXA Art Insurance, that generously donated the painting and funding for the research; special thanks go to Chris McGlinchey at the MoMA, New York.

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