Laser spectroscopic and optical imaging techniques in chemical and structural diagnostics of painted artwork

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The preservation of our cultural heritage provides us with a source of invaluable information on history and civilization. Uncovering the rich artistic, cultural, and historical information often contained in works of art requires an interdisciplinary and systematic approach. One essential component of such an approach is the use of analytical techniques for the physical, chemical, and structural characterization of artwork. Indeed, analytical chemistry offers a significant contribution to the field of artwork analysis, especially with the advent of powerful analytical techniques and instrumentation that have been applied to a variety of problems encountered, ranging from the identification of pigments, binders, and varnishes to dating, provenance, and authentication.[1–3] Despite their high degree of sophistication, many modern analytical techniques suffer from the major drawback that they are not applicable to in situ analysis and require sampling, which unavoidably leads to permanent damage of the object of art. Given the value and sensitivity of artwork, the development of flexible, portable instrumentation that can provide analytical information in situ is highly desirable.

Another important aspect in artwork analysis is the ability to assess the spatial distribution of chemical components across the surface of an object. This can be achieved by implementing a scanning approach combined with a nondestructive in situ spectroscopic technique, but this can be both complicated and time consuming. On the other hand, a spectroscopic imaging approach capable of recording images within selected narrow spectral bands and across a broad wavelength range appears to be an attractive alternative. Imaging analysis, to date, has been essentially limited to the photographic examination of artwork, using various illumination sources and types of filters and film. The analytical capabilities of imaging techniques can be greatly improved with the combination of state-of-the-art digital charge coupled device (CCD) cameras and imaging monochromators that capture a series of images at different wavelengths within a wide spectral range, or even record a full spectrum per image pixel.

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This paper presents examples of laser-induced breakdown spectroscopy (LIBS) and laser-induced fluorescence (LIF) spectroscopy implemented for the analysis of artwork.[4,5] In addition, the analytical capabilities of a multispectral imaging system (Mu.S.I.S. 2007), designed and developed at the Foundation for Research and Technology–Hellas (FORTH) Institute of Electronic Structure & Laser (IESL) (Heraklion, Greece) (*Figure 1*) for the 2-D analysis and documentation of painted artwork, are briefly outlined.


Figure 1 *Mu.S.I.S. 2007 system.*

LIBS is a simple and rapid atomic emission spectroscopic technique for elemental analysis of materials that is characterized by high sensitivity and selectivity.[6] The focusing of an intense nanosecond laser pulse on the surface of the sample results in plasma formation, which, upon cooling, emits radiation (fluorescence from excited atoms and/or ions) characteristic of the elements contained in the sample. Because most pigments used in paintings, from antiquity to date, are either metal oxides or salts, LIBS appears to be a suitable technique for pigment identification. The technique has several key advantages important to its application in artwork analysis. In particular, it requires no sample removal or preparation and therefore can be performed in situ on the artwork itself. The laser beam is focused to a tiny spot, and, as a result, extremely small quantities of sample material are consumed (of the order of less than 1 μg) and the analysis can be characterized as practically nondestruc-

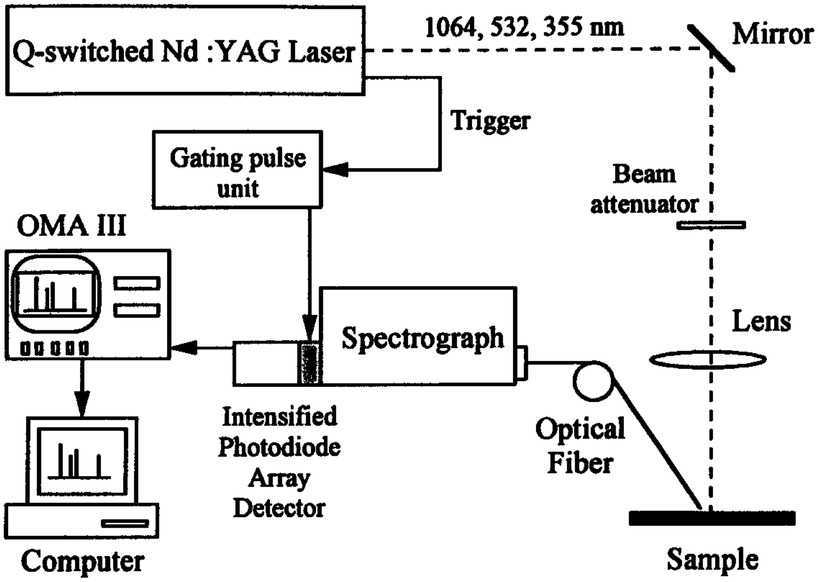

Figure 2 *Schematic diagram of the experimental setup used for the LIBS and LIF measurements.*

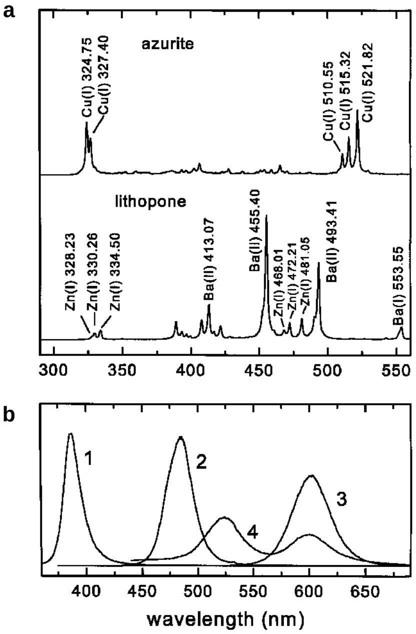

Figure 3 *a) LIBS spectra from lithopone ($ZnS{\cdot}BaSO_4$) and azurite ($2CuCO_3{\cdot}Cu(OH)_2$). Laser wavelength: 1064 nm. b) Laser fluorescence emission spectra of 1) zinc white, 2) cadmium yellow lemon, 3) cadmium red, and 4) a mixture of cadmium orange and cadmium red. Excitation at 355 nm.*

Table 1

Selected pigments examined and corresponding analytical data

Pigment	Chemical formula	Elements identified by LIBS	Fluorescence emission (λ exc: 355 nm)
Lead white	$2PbCO_3{\cdot}Pb(OH)_2$	Pb	
Titanium white	TiO_2	Ti	
Zinc white	ZnO	Zn, Ba, Ca	λ_{em}: 390 nm
Lithopone (white)	$ZnS{\cdot}BaSO_4$	Ba, Zn, Ca	
Azurite (blue)	$2CuCO_3{\cdot}Cu(OH)_2$	Cu	
Ultramarine blue	$3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2Na_2S$	Al, Na	
Cobalt blue	$Co_2O_3{\cdot}(Al_2O_3)$	Co, Al	
Malachite (green)	$CuCO_3{\cdot}Cu(OH)_2$	Cu	
Chromium green	Cr_2O_3	Cr, Pb, Ba, Ca	
Cadmium yellow lemon	$Cd_{0.9}Zn_{0.1}S{\cdot}BaSO_4$	Cd, Ba, Zn	λ_{em}: 490 nm
Chromium yellow	$PbCrO_4$	Cr, Pb, Ba, Ca	
Cadmium orange	$CdSe_xS_{1-x}$	Cd	λ_{em}: 566 nm
Cadmium red	$CdSe_{0.3}S_{0.7}$	Cd	λ_{em}: 600 nm
Cinnabar (red)	HgS	Hg	
Lead red	Pb_3O_4	Pb	

tive. In addition, because of the tight focusing, spatial resolution is achieved, both across the surface of the work and in depth, allowing for studies of surface inhomogeneities and depth profile analysis, respectively, thus providing nearly microscopic information.

LIF, a versatile, nondestructive analytical technique, can be performed in situ, and provides information that can be directly related to the molecular structure of pigments or other components of paintings, both organic and inorganic. Excitation of the sample with a low-intensity continuous wave (cw) or pulsed laser beam produces the emission of fluorescence (more generally luminescence) that can be, for instance, characteristic of a pigment or provide information on the aging of the binder or the varnish.

Mu.S.I.S. 2007 is a patented, digital imaging system that was developed to improve and integrate several imaging techniques. The modular system is useful for the scientific analysis of artwork. Upon appropriate illumination of an object, the system is capable of recording diffuse reflectance and/or fluorescence emission black and white images in several spectral bands from the UV to the near infrared (NIR), or combining imaging bands that result in color or pseudocolor (false-color infrared) imaging. This allows for accurate documentation and quantification of the optical information. In addition, important analytical information can be obtained, since the system can differentiate between selected pigments having the same color appearance in the visible, but different fluorescence and/or diffuse reflection spectral characteristics outside the visible band, due to their different chemical nature.

Experimental

The experimental arrangement used for both LIBS and LIF is schematically depicted in *Figure 2*. The main components of the setup are a nanosecond pulsed laser, appropriate beam delivery optics, and spectrum acquisition system. In a typical LIBS experiment, a nanosecond Q-switched Nd:YAG laser operating at its fundamental (1064 nm) or harmonic frequencies (532 nm, 355 nm) is employed. The laser beam is focused on the sample surface by means of a convergent lens (typical focal length 50–150 mm). A single laser pulse of energy ranging from 2 to 20 mJ/pulse is used for each measurement producing strong emission signals. Because of the value and sensitivity of the objects studied, work is deliberately done at lower than usual power density values (0.2–2 GW/cm^2) without sacrificing spectral quality and S/N. The light emitted is collected with an optical fiber into a 20-cm focal length spectrograph (PTI model 01-002AD, **Photon Technology International,** Monmouth Junction, NJ) equipped with two holographic gratings of 1200 and 300 lines/mm, for high and medium spectral resolution measurements, respectively. The detector is an Optical Multichannel Analyzer (OMA III system, **EG&G PARC** model 1406 [Princeton, NJ] with an intensified photodiode array detector, **EG&G PARC** model 1420UV) that permits fast grating with adjustable delay and gate width.

The same experimental arrangement is used for fluorescence analysis; the excitation is usually provided by the third harmonic (λ = 355 nm) of a nanosecond Q-switched Nd:YAG laser and the incident to the sample laser beam is properly attenuated and unfocused. The emitted molecular fluorescence is collected and recorded on the same detection system.

The Mu.S.I.S. 2007 is essentially an imaging detection system that covers a wide spectral range (320–1550 nm), and employs an appropriate combination of a cooled CCD optical detector and an infrared-to-visible imaging converter (cesium–silver oxide). Images are captured, in several spectral bands within this wide spectral range, with the aid of a computer-controllable imaging band selection mechanism, while the captured images are digitally acquired and displayed in real time on a computer monitor. Specially developed software is employed for the camera sensitivity, image acquisition, calibration control, image analysis, and data handling. In any imaging band,

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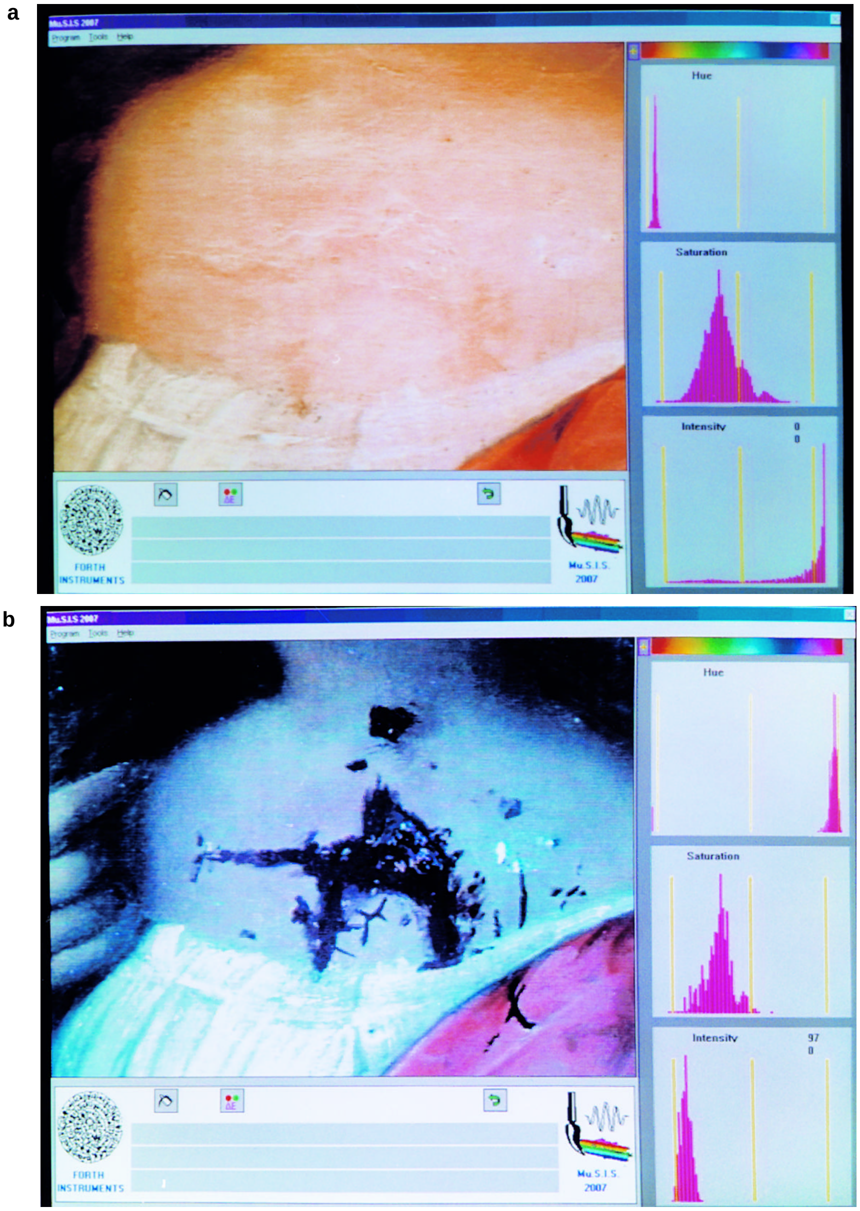

Figure 4 *Detailed color image (a) and fluorescence image (b) from the painting "La Bella." Color parameter histograms in a standard color space are shown next to the images.*

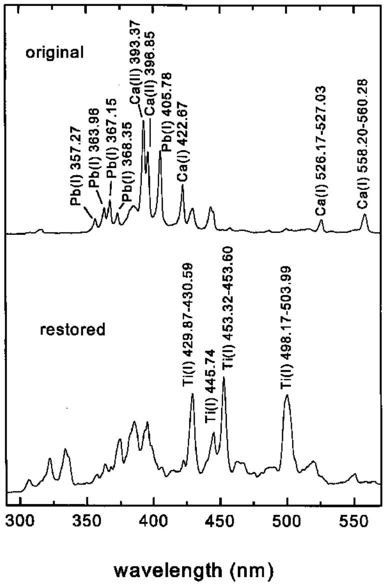

Figure 5 *LIBS spectra from original paint and from paint in restored areas of the oil painting.*

the intensity of the captured light is recorded on a gray scale for each image pixel. In color imaging, the modeling of the optical information is based on standardized color spaces.[7] The reproducibility of the image capturing procedure is ensured with the aid of an effective calibration method,[8] which is employed in all imaging modes, using appropriate calibration specimens. The system also enables the quantitative comparison of previously stored fluorescence and/or diffuse reflection characteristics of standard pigment samples with those measured during actual artwork examination, providing information for pigment identification.

Results and discussion

In order to establish spectral characteristics of the various pigments and identify spectral features of analytical importance, measurements were performed on a variety of modern and old pigments (*Table 1*). LIBS spectra were collected from samples in powder form as well as from model oil painting samples. Spectra from selected pigments examined are shown in *Figure 3a*. In the LIBS spectra, several characteristic atomic emission peaks are used to identify the elements present. Most pigments provide clean LIBS spectra with emission lines that are easy to assign even with the use of the medium-resolution grating in the spectrograph. In certain cases, use of a high-resolution grating clarified or simply confirmed the results obtained at low resolution. LIBS spectra taken from oil painting samples showed that the interference from the organic matrix appeared to be minimal in all cases.

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The same samples were examined with respect to their fluorescence behavior. A limited number of pigments (zinc white, a wide variety of cadmium sulfoselenide-based pigments, and some organic pigments) exhibited fluorescence emission (Figure 3*b*). The spectra recorded are rather broadband; however, they are characteristic of the pigments examined and can be used to identify these pigments.

Several painted works of art have been examined with the techniques described here. An example is presented in which spectroscopic and imaging data revealed several interesting features during the systematic study of a late eighteenth-century oil painting on canvas (copy of Palma Vecchio's "La Bella," National Gallery of Athens, Greece) which has been subjected to partial restoration. A detailed imaging analysis was performed operating the Mu.S.I.S. 2007 in several spectral bands and modes. This examination identified certain areas on the painting that had been subjected to restoration, and differentiated those with respect to the original by means of fluorescence

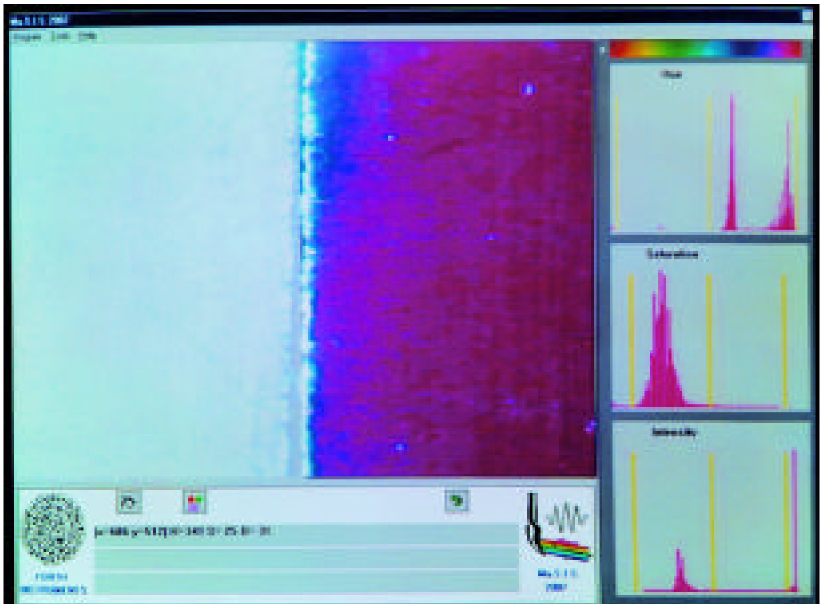

Figure 6 *Fluorescence image from model oil paint samples of titanium white (right) and lead white (left) along with color parameters.*

and NIR reflectance imaging. For example, *Figure 4a* shows a detail of the painting (color image), while Figure 4*b* shows the visible fluorescence image of the same detail (employing excitation at 365 ± 10 nm). The fluorescence image clearly differentiates the area in which retouching has been performed with respect to the general background fluorescence. Obviously the retouching was done with pigments having the same color appearance and as a result is invisible to the human eye. However, the different fluorescence behavior suggests a different chemical composition between the original pigments and those used for restoration.

In order to identify the pigments, LIBS analysis was performed at a few selected points on both the original and retouched areas of the painting. The spectra obtained clearly uncover the chemical differences of the retouched areas with respect to the original areas, indicating the existence of lead white in the original (characteristic lead emission lines in the spectrum) and titanium white (characteristic titanium spectral features) in the retouched parts of the painting (*Figure 5*).

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In parallel, further fluorescence imaging studies were performed on model oil paint samples of lead white and titanium white. *Figure 6* shows the fluorescence images of the titanium white and lead white model samples as well as the corresponding color histograms. The color characteristics of the pigments in the model samples very closely match those of the original and retouched areas in the painting. These findings suggest that the restoration was performed in this century, since titanium white did not become commercially available until after the early 1900s.

Conclusions

Laser spectroscopic techniques such as LIBS and LIF offer the possibility for performing in situ analysis on works of art and require no sampling. The main strengths of LIF are simplicity, speed, sensitivity, ability to analyze both organic and inorganic materials, and, more importantly, nondestructiveness. The LIBS technique combines simplicity, versatility, sensitivity, and selectivity, while it can provide depth profiling information illuminating the stratigraphy of a painting. The Mu.S.I.S. 2007 imaging system features spectral imaging capabilities across a very broad spectrum ranging from the UV to the NIR and can provide rich information regarding the structure of painted artwork as well as the type of materials used.

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The collaboration of Mr. M. Doulgeridis from the Conservation Department of the National Gallery of Athens (Athens, Greece) is gratefully acknowledged. This work was partially supported by Laser Technology in the Conservation of Artworks, project no. 640 of the EPET II Program (Greece) from the EU Structural Funds and by the Ultraviolet Laser Facility operating at FORTH under the TMR Program (DGXII, ERBFMGECT 950021) of the EU.