

Standoff laser spectroscopy for wall paintings, monuments and architectural interiors

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Abstract

Multimodal analysis using complementary imaging and spectroscopic techniques is being increasingly adopted for the examination of materials in cultural heritage. However, practical limitations, such as inaccessible heights, hinder the use of conventional mobile instruments for in situ analysis of wall paintings. This paper presents a novel mobile standoff laser spectroscopy system that can operate in the range of 3–15 m. Small area standoff macro-

INTRODUCTION

Complementary multi-technique imaging and spectroscopic analysis are being commonly adopted for the examination of materials in cultural heritage. However, in situ analysis of wall paintings with currently available mobile instruments is often hampered by inaccessible heights (Vandenabeele et al. 2014). Following our previous development and application of a remote spectral imaging system, PRISMS (Liang et al. 2014), that operates at tens of metres from an object of interest, a new mobile standoff laser spectroscopy system was developed to work in the 3–15 m range for high-resolution automated imaging over a large scale.

The remote laser spectroscopy system consists of Raman spectroscopy and laser-induced breakdown spectroscopy (LIBS). Raman spectroscopy is a commonly used laser technique for material identification, as it identifies molecular structural fingerprints by observing spectral shifts from the excitation laser wavelength resulting from molecular vibrations. A standoff Raman system has recently been developed and implemented that operates from a distance of 3–15 m (Li et al. 2019). However, since single-point analysis cannot satisfy certain demands in conservation research, e.g. analysing the distribution of painting materials across an area, the remote Raman system was upgraded to automatically map a macroscopic area (> a few square centimetres) at standoff ranges. An in situ analysis of a wall painting in the Music Room of the Royal Pavilion in Brighton (UK) is presented as proof of concept, helping to evaluate the feasibility of the implementation and potential applications of macro-Raman mapping. Before applying Raman mapping to the scanning of artworks, the priority was to confirm the safe use of the instrument by verifying the potential risk of laser-induced degradation for a laser-based technique that covers a relatively large area.

LIBS, on the other hand, is micro-destructive and detects characteristic atomic emission lines for different elements from the plasma created by high-power laser pulses on a tiny spot (~1 mm). The combination of Raman and LIBS can provide complementary material information about an artwork (Burgio et al. 2001, Bruder et al. 2007).

The system is flexible enough to perform the following operations: 1) non-invasive standoff Raman spectroscopy; 2) standoff macro-Raman mapping; 3) combined standoff Raman/LIBS analysis at selected spots where it is ethically justified to take micro-destructive measurements.

Raman mapping was performed in situ on a wall painting in the Royal Pavilion in Brighton, UK. The safety of standoff macro-Raman mapping with regard to laser-induced degradation was evaluated on paint samples made from a range of common pigments. In addition, the combination of Raman spectroscopy and laser-induced breakdown spectroscopy (LIBS) enabled the depth-resolved study of multi-layered paintings, revealing elemental and molecular information for each layer.

Employing these two complementary techniques, both molecular structure and elemental composition information are acquired at the same position on a sample, which when combined with the remote reflectance spectroscopy information provided by PRISMS, is a powerful means of obtaining material identification, since in many cases a single technique is not sufficient to provide a definitive answer. The advantage of this system is the ability to carry out standoff measurements in which personnel and instruments are positioned on the ground at significant distances from the target. This is ideal for wall paintings, large architectural interiors (churches, temples, palaces and large caves), large sculptures, monuments and archaeological sites.

INSTRUMENTATION

Careful consideration was given to the system's design to meet the special needs for the study of wall paintings. Raman spectroscopy operates with a continuous wave (CW) laser at 780 nm, while LIBS uses a 1064 nm pulsed laser for ablation. Telescopes are used for the collection of the Raman and LIBS signals.

The original configuration of a mobile long-range standoff Raman spectroscopy system developed in-house was described in detail in an earlier publication (Li et al. 2019). The system uses a 780 nm CW laser source, a Maksutov-Cassegrain telescope and a spectrograph coupled with a cooled (-70°C) CCD detector. The laser beam is made co-axial with the telescope using a pair of mirrors. The entire system is mounted on a motorised telescope mount operated by bespoke software that synchronises the motions of the laser beam and the recording of the spectra. The output beam is collimated with a slight divergence resulting in a spot size of ~ 4 mm at 4 m on the target. The maximum laser power at sample is 48 mW, which translates to an irradiance of 0.38 W/cm^2 .

The LIBS system employs a 1064 nm pulsed laser (15 Hz repetition, 50 mJ pulse energy, 5–7 ns pulse width). The focussed beam size is 1 mm in diameter on the target. Designed with an oblique geometry, a telescope is used to collect the reflected light. A fibre is attached to the rear port of the telescope to send the signals to a spectrometer. With a maximum pulse energy of 50 mJ, the peak intensity of the laser pulse at sample level can reach 1.27 GW/cm^2 .

Table 1 compares the intensity and fluence of light sources used in this standoff laser spectroscopy system. The laser intensity is 3–5 orders of magnitude lower than benchtop micro-Raman instruments commonly used with artworks, therefore the risk of laser-induced degradation is significantly reduced (Li et al 2019).

Table 1. Light intensity and fluence comparison

	P_{av} (mW)	P_{max} (W)	Spot size (μm)	Dwell time (s)	I_{av} (W/cm^2)	I_{max} (W/cm^2)	Fluence (J/cm^2)
Micro-Raman	0.01–1		1	1	$(1.27\text{--}127) \times 10^3$		$(1.27\text{--}127) \times 10^3$
Standoff Raman	48		4000	10–1800	0.38		3.8–684
LIBS		$(4\text{--}100) \times 10^5$	1000	5×10^{-9}		$(5.10\text{--}127) \times 10^7$	0.25–6.37

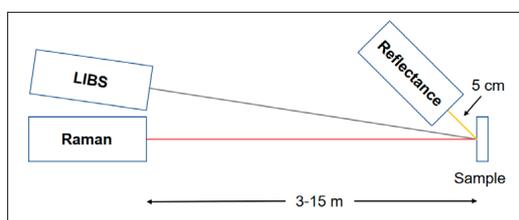


Figure 1. Experimental setup for the measurement of laser-induced degradation and depth-resolved analysis of the paint samples

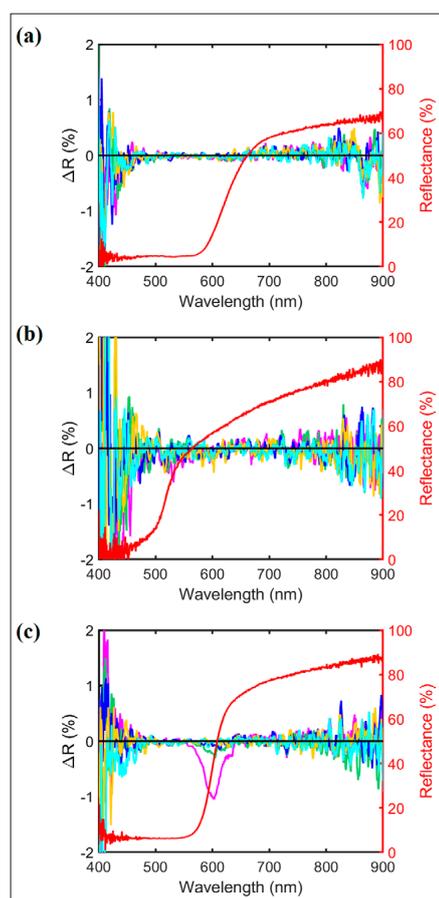


Figure 2. Difference spectra for reflectance of: (a) a cochineal lake oil paint after 6 minutes of irradiation at full power; (b) a chrome yellow (medium) oil paint after 6 minutes of irradiation; (c) a vermilion (light) oil paint after 6 minutes of irradiation. Laser irradiation was carried out by a collimated beam with a 4 mm diameter and 48 mW of power at sample level. The red lines represent the reflectance of the corresponding pigment samples

PERFORMANCE EVALUATION

Lab tests on over 50 common pigments in various binding media (animal glue, linseed oil and egg tempera) showed that the standoff Raman system can detect the majority of them within 10 seconds and almost all of them, with the exception of some green pigments, within 30 minutes (Li et al. 2019). The system is capable of indoor daytime operations in standoff scenarios with natural light (daylight through windows) and can quickly respond to the changing daylight throughout the measurement with automatic online daylight subtraction (Ibid.). In comparison with conventional benchtop micro-Raman instruments, the signal-to-noise ratios (SNR) are comparable at 4 metres in a given integration time.

EXAMINATION OF LASER-INDUCED DEGRADATION EFFECTS

A combined setup consisting of the long-range standoff Raman system and a fibre optics reflectance spectroscopy (FORS) system in a local setup, as shown in Figure 1, was used to investigate the laser degradation effects. The laser beam irradiated the vertically placed sample at normal incidence, while a retro-reflection probe was aligned at a 45° angle to the laser beam to collect the spectra before and after laser irradiation. A low-power tungsten halogen light (Mikropack DH-2000) was used as the illumination source for FORS. A retroreflective probe like that mentioned in Liang et al. 2013 was used with the FORS, which gives a focussed elliptical spot of 0.45 mm by 0.75 mm at sample level. The reflectance spectra were collected by a spectrometer (Ocean Optics HR2000) at an integration time of 200 ms, at an average of 10 times, amounting to 2 seconds per measurement.

A range of historic artist's oil paint samples were examined for laser-induced degradation risks by taking reflectance spectroscopy measurements before and after Raman measurements. The selection included organic and inorganic pigments varying in absorption at the laser excitation wavelength. All of the samples were oil based and painted in 2006–2007 on plywood boards with white gesso substrate in rabbit skin glue (Liang et al. 2013).

Before the laser irradiation, three reflectance spectra were recorded successively for each sample. A series of Raman spectra were then acquired. Right after laser irradiation, a series of reflectance spectra were collected over a period of 5 minutes. To make sure that no other factors interfered with the degradation tests, another set of measurements were taken as the control beforehand using an identical procedure but without the laser irradiation.

For cochineal lake and chrome yellow, no damage was detected after 6 minutes of irradiation, as shown by the change in the reflectance spectra collected before and after (Figure 2a and 2b). The vermilion sample showed signs of alterations after 6 minutes of irradiation (Figure 2c), with changes of ~1% in reflectance around 599 nm. Interestingly, reversions were observed over a time period of 1 minute and eventually settled down to the original spectrum, indicating a temporary rather than a permanent alteration. Raman spectra, however, did not show any changes, which may suggest that either the temporal changes did not correspond to an alteration

in the crystalline structure or that Raman was not sensitive enough to detect the small change. It is worth noting that the laser intensity in the standoff Raman configuration is 3–5 orders of magnitude lower than that typically used in the micro-Raman examination of artworks.

STANDOFF MACRO-RAMAN MAPPING

Macro-Raman mapping is similar to micro-Raman mapping except the field of view is larger and the spatial resolution is lower. Standoff Raman allows in situ macro-mapping. Mapping an area of a wall painting could help investigate the spatial distribution of various pigments and degradation products or monitor the degree of degradation on a macroscopic scale.

An in situ application was carried out in the Music Room of the Royal Pavilion in Brighton, UK, as part of a larger campaign using a suite of non-invasive imaging and spectroscopic techniques offered by ISAAC mobile lab (www.isaac-lab.com/available-techniques). The Royal Pavilion was built for George IV. Work commenced in 1787 and the building was extended and completed by the architect John Nash in 1815. The music room was originally designed by Frederick Crace, George IV's chief decorator, in the chinoiserie style (Loske 2014). The room is completely decorated with floor to ceiling murals depicting Chinese landscapes. The oil-on-canvas paintings were completed in 1820 and were originally stretched and tacked onto the lathe and plaster walls. Historic accounts reveal that in 1821, issues of damp on the walls were causing problems and some of the murals were removed and repaired. The plaster walls were restored and the murals were then re-hung. By 1850, the murals, along with many other objects, fixtures and fittings, were rolled up and removed by Queen Victoria and taken to London. In 1864, the murals were returned by Victoria and this time were directly glued onto the plaster walls. The care and conservation of the music room murals is obviously an ongoing concern. A better understanding of the materials and techniques and interventions would allow informed decisions for any future conservation work. The room is over 12 metres in height and was previously only accessible for examination by scaffolding.

An area of 1.2 by 1.2 cm was selected for macro-Raman mapping at a distance of 4 metres (Figure 3a). The shortwave infrared (SWIR) (1000–2500 nm) reflectance spectra for the scanned area showed that the binding medium was consistent with oil. The Raman maps acquired in this area, and typical Raman spectra representing the three colours, are shown in Figure 3b and 3f. The mapping consisted of 25 spectra (5 by 5) within the area, ensuring that adjacent points were overlapping with a step size of ~2.5 mm, given that the spot size was about 4 mm. At each point, the Raman spectrum was collected using a 180 seconds integration time and two accumulations for cosmic ray removal. Despite the presence of fluorescence in the spectral background due to the oil binder, vermilion was identified by peaks at 252 and 343 cm^{-1} , in all red, orange and yellow areas. Chrome yellow was present with a characteristic band at 841 cm^{-1} , in both yellow and orange areas. No other orange pigments were detected. Therefore, the orange area was most likely a combination of vermilion and chrome yellow.

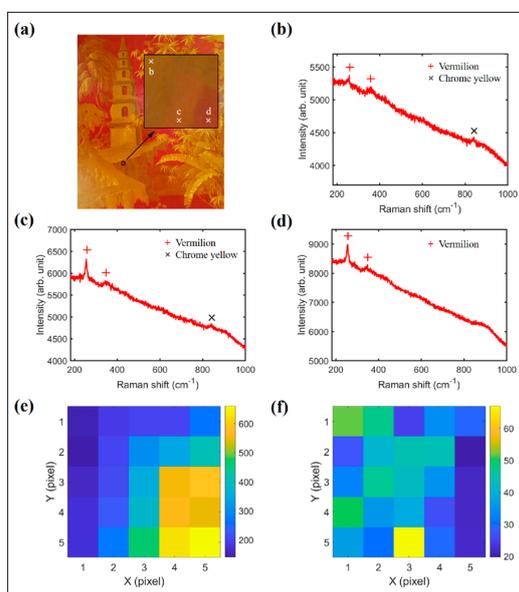


Figure 3. (a) A colour image showing the area selected for standoff macro-Raman mapping; (b) a typical Raman spectrum representing the yellow area (see position 'b' marked on (a)); (c) a typical Raman spectrum representing the orange area (see position 'c' marked on (a)); (d) a typical Raman spectrum representing the red area (see position 'd' marked on (a)); vermilion peaks are marked as +, while chrome yellow signals are marked as x; (e) map for vermilion identified in the area; (f) map for chrome yellow identified in the area

DEPTH-RESOLVED ANALYSIS OF MULTI-LAYERED PAINTINGS

Regarded as being micro-destructive, LIBS is normally used only when it is necessary to provide confirmation of material identification where other standoff techniques cannot give definitive answers. On the other hand, the destructive nature of LIBS can be exploited to ablate the materials. Combined with Raman spectroscopy, depth-resolved molecular and elemental information can be provided at the same time when analysing the same spot using successive laser pulses (Bruder et al. 2007, Kaszewska et al. 2013).

A multi-layered mock-up sample was designed and prepared in the lab for testing. Similar to the samples used for degradation tests, it was painted on a plywood board with white gesso substrate. From bottom to top, indigo, vermilion and red lead layers in animal glue were painted successively, as shown in Figure 4a. The multi-layered paint sample was placed vertically at 5 metres from the instruments where standoff Raman and LIBS systems were set up abreast in an oblique design (Figure 1). Both the Raman laser and the ns-pulsed laser for LIBS were focused on the same roughly 1 mm diameter spot. For LIBS, a typical measurement requires only one laser pulse on a timescale of several nanoseconds, and the spectrum is then acquired in less than one second. The experimental procedure started with a Raman measurement with a 10 second integration time and three accumulations for cosmic ray removal, followed by a single LIBS laser shot.

A total of 70 successive spectra were obtained by alternating LIBS and Raman measurements. Microscopic images of the final crater are shown in Figure 4b and 4c. The edge of the crater shows that the successive paint layers and the vermilion layer were clearly burnt (Figure 4c). A virtual cross-section image of the final crater was taken with an 810 nm ultra-high-resolution optical coherence tomography (OCT) system (Figure 4d) (Cheung et al. 2015). With Raman, the 780 nm laser used for excitation penetrated the top layer and revealed material information below, which made it difficult to distinguish between the layers. It was observed that

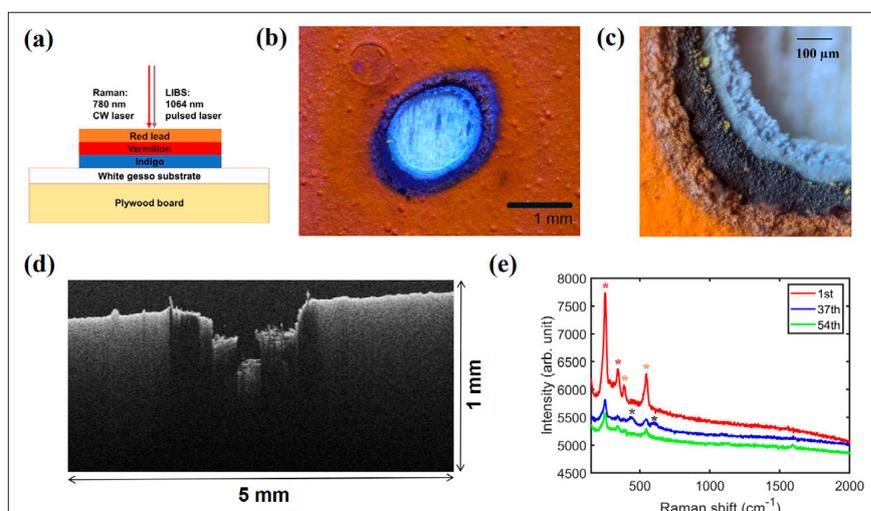


Figure 4. (a) Schematic of a multi-layered paint sample prepared for the depth-resolved analysis; (b) the crater formed after 70 shots of 50 mW laser pulses; (c) details of the edge of the damage crater; (d) 810 nm ultra-high resolution OCT image taken over the ablation crater after 70 laser pulses; (e) Raman spectra before the 1st (red), 37th (blue) and 54th (green) 1064 nm laser pulse; an offset of 150 was added to the blue curve for clarity; vermilion peaks are marked as red asterisks; red lead peaks are marked as orange asterisks; rutile peaks are marked as black asterisks

before the 1st shot, strong red lead (388 and 546 cm^{-1}) and vermilion (252 and 343 cm^{-1}) signals were detected (Figure 4e), and these continued to be detected even after the 70th shot. Two peaks at 444 and 608 cm^{-1} appeared in the 37th spectrum, indicating the presence of rutile (titanium dioxide, TiO_2), which was found to be present in the white gesso substrate by another direct Raman measurement on the white substrate. After 42 pulses, a weak peak at 1592 cm^{-1} appeared, which could be assigned to lignin from the plywood board as the wood layer was revealed.

After the 2nd shot, LIBS revealed higher signal intensity for Pb compared to the 1st shot (Figure 5b). The 1st shot normally removed the dust and other impurities from the sample surface. A strong peak at 405.9 nm and a quadlet at $357\text{--}373\text{ nm}$, as well as several weak peaks characterising Pb, were detected. The evolution of intensities for the main peaks of four elements, i.e. 405.9 nm for Pb in red lead (Pb_3O_4), 546.1 nm for Hg in vermilion (HgS), 393.3 nm for Ca in chalk (CaCO_3) and 334.9 nm for Ti in rutile (TiO_2), are shown in Figure 5a. Up to the 7th pulse, it appeared that ablation material characterised by Pb originated from the top red lead layer. As the penetration depth increased with successive shots, transitions from layer to layer were observed. For instance, while transitioning from the red lead to vermilion layer between shots 7–14, the Hg line intensity increased substantially (Figure 5c) and stayed more or less constant until the 28th shot when it started to decrease (Figure 5d). In the meantime, Ca line intensity increased significantly (Figure 5e). The Ti signals started to appear after the 29th shot and peaked at the 38th shot. Hg intensity fell sharply after the 37th shot. After 41 shots, the Ca signal dropped rapidly. After 47 shots, the intensity of all four elements tended to zero, though trace Ca and Ti could still be detected until the end (Figure 5f).

Combining the Raman and LIBS results, it became clear that there was a thin red lead layer followed by a thicker vermilion layer. The only puzzle was the curious depth distribution of Ca, as shown in Figure 5a. The source of calcium in the paint layers was likely to be the animal glue which was used as the binder. X-ray fluorescence (XRF) spectroscopy confirmed the presence of Ca in the dried animal glue powder ($\sim 2.3\text{ wt}\%$) and indigo ($\sim 26.4\text{ wt}\%$), but not in any other pigments. The first Ca peak followed

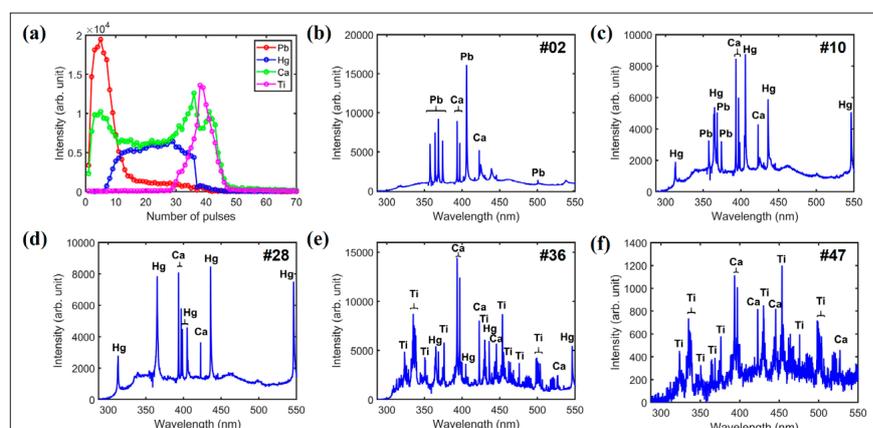


Figure 5. (a) Evolution of the line intensities for four selected peaks (Pb 405.9 nm , Hg 546.1 nm , Ca 393.3 nm and Ti 334.9 nm) for increasing shot sequence; (b) emission lines obtained after 2 laser pulses; (c) emission lines obtained after 10 laser pulses; (d) emission lines obtained after 28 laser pulses; (e) emission lines obtained after 36 laser pulses; (f) emission lines obtained after 47 laser pulses

that of Pb, which suggests that the Ca came from the binder (animal glue) of the red lead. The Ca content remained stable for the vermilion layer, shown by the flat peak of Hg up until the 28th shot. After the 29th shot, the Ca intensity started to increase with the simultaneous decline of Hg and increase of Ti, indicating a transition from the vermilion layer to the next layer. There was a small Ca peak at the 31st shot which might be due to the Ca-rich indigo layer. However, indigo was not detected by Raman, which may be because it was so thin that it was ablated by just one shot. It is worth noting that LIBS revealed some layer information on the white gesso substrate that was previously unknown. Reflectance spectroscopy (350–2500 nm) confirmed the presence of calcite (chalk) and gypsum. A comparison of the Ti (which peaked after the 38th shot) and Ca (which peaked at the 36th and 41st shots) curves suggests that the white gesso substrate was composed of a Ca-rich layer of chalk and gypsum above a layer of rutile and then another chalk and gypsum layer.

CONCLUSION

A long-range (up to 15 metres) Raman spectroscopy system using a CW laser source at 780 nm demonstrated that it was able to perform standoff macro-Raman mapping that complemented long-range standoff visible and near-infrared spectral imaging, which is routinely employed for pigment identification by our ISAAC mobile lab. Prior to the in situ measurements, the safe use of this standoff laser technique on artworks was discussed in terms of laser intensity (3–5 orders of magnitude lower than the range of intensities used in micro-Raman analysis of artworks) and verified by experiments where a reflectance spectroscopy system was used to examine the laser-induced degradation effects on a range of common pigments. The setup with a collimated beam was shown to be able to operate safely for all of the pigments tested. Although alterations were detected immediately after laser irradiation for some pigments, reversions were observed shortly afterwards, indicating a non-permanent process. The complementarity of standoff Raman and LIBS revealing elemental and molecular information was demonstrated by a unique application where depth-resolved analysis of a multi-layered paint sample was performed.

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