e-PRESERVATIONScience

e-PS, 2015, **12**, 14-19
ISSN: 1581-9280 web edition
ISSN: 1854-3928 print edition

e-Preservation Science (e-PS)

is published by Morana RTD d.o.o.
www.Morana-rtd.com

SCIENTIFIC PAPER

INVESTIGATION OF ULTRAFAST PICOSECOND LASER SYSTEM FOR CLEANING OF METAL DECORATIONS OF 17TH C. GLOVES OF KING CHARLES I

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Abstract

The potential and feasibility of using ultrafast picosecond laser scanning pulses (1064 nm) for the removal of tarnish over metal threads of the gloves worn by king Charles I (1600 –1649, England) were investigated. Analytical techniques including optical microscope, SEM-EDX and Raman Spectroscopy were employed to characterize the constituent materials of the gloves and their condition, and to assess the cleaning results obtained. Following the trails of optimization tests of laser cleaning parameters, results suggest that satisfactory laser cleaning could be achieved for the removal of tarnish without damage the underlying metal threads substrate. Considerations for the application of ultrafast ps laser cleaning are presented which highlight the advantages of applying ultrashort laser processing for cleaning composite material with consideration of the limitations regarding the current practical application of ultrafast laser processing for the conservation of cultural heritage.

1 Introduction

One of the most problematic processes is the cleaning of composite object; the different materials hence may need to be cleaned using safe and precise methods. Gloves, purportedly belonging to Charles I (17th C, Great Britain), enriched with valuable mixture of materials such as embroidered metal threads in textile, are the focus of this study. The selected historic gloves were subject to atmospheric pollutants and dust in uncontrolled museum environment. Silver threads are particularly sensitive to tarnishing or oxidation due to the presence of pollutions gases such as hydrogen sulphide, which interact with silver and produce silver tarnish (Ag_2S), while whiting of silver could be induced by reaction between silver and oxygen with the formation of Ag_2O.[1,2] Furthermore, gilt silver threads-containing copper can corrode preferentially by chloride salts and form cuprous chloride.[3,4] Condensation of water vapor (over dust) may be another significant factor within museums with limited environment control.[5] Dust particles deposited on the museum objects are abrasive and hygroscopic and can also encourage the microbial growth.[6] Cleaning of the gloves is a necessity to improve the aesthetic appearance of the metal decorations and designs used on royal accessories and maintain its long-term stability. However, the potential need for other proposed conservation procedures, such as stabilization of loosen metal strips and redisplaying, may require the prior removal of surface tarnish. In this work, laser cleaning was proposed for the cleaning of composite gloves due to the difficulty of removing unwanted materials from multi-composition material using traditional methods which could be harmful to metal decorations, skin and dyed textile.[7] Laser has been used successfully, comparing with traditional methods, to clean some examples of metal threads accompanied with embroidery.[8-10] Lasers with ultrashort pulse duration are expected to reduce thermal diffusion effects due to the reduced contact time between the laser pulse and the substrate being cleaned. The practicability and effectiveness of ultrashort lasers for cleaning artworks has demonstrated before with satisfactory results.[11,12]

received: 04/11/2014

accepted: 15/03/2015

key words:
metal threads, tarnish, SEM-EDX, picosecond; cleaning, optimization

While most of the common mechanical, wet and chemical cleaning techniques used in cleaning textiles show higher risks and could be incompatible for composite materials which have delicate organic and inorganic substrates.[13,14] In contrast, the main advantage of laser cleaning may be that lasers do not interact mechanically with the delicate substrates and risk of damage could be reduced.[6-8] Past studies,[5,8] of laser cleaning of metal threads using the nanosecond UV lasers showed better cleaning results with could be achieved with wavelengths 193 nm and 355 nm and some side effects such as discoloring caused by longer wavelengths emitting at 532 nm.[7] Recently, the development of industrial applications of laser technology offers the option of ultrashort pulse durations which used successfully to prevent thermal and mechanical side effects.[15] However, ultrashort pulse duration of the picosecond laser system will lead to low volume of material ablated (nano and micro size scales) from the object surface per pulse which provides high precise and ultra-fine cleaning. The aim of this work is to investigate the feasibility and effectiveness of ultrafast and precise computed-scanning picosecond laser (1064 nm) with a repetition rate of 10 kHz and a temporal pulse length of 10 ps for the removal of tarnish over metal threads of delicate museum composite material using microscopy and elemental analysis.

2 Materials and methods

2.1 Object

The selected object is pair of gloves and displayed in Ripley's Museum (London, UK). The gloves are associated with documentation attesting to the fact that they were once possessed by Charles I (1600 –1649, Figure 1). The leather of the gloves is made of soft-cream whitish skin and the seams of the fingers and thumbs are very finely sewn. The gauntlets are heavily embroidered with metal threads and spangles in red-dyed textile, while the outer edged trimmed with applied metal thread fringes. Different forms of metal threads have been recorded (Figure 2); metal strips wound around a fibre core, round-shape spangles and metal wires wound around threads of fibre core. Gauntlets have an inner lining of pink taffeta and there is an interlining of coarse linen to stiffen the gauntlets. The gloves have a stylish design and flowers embroidered in pink, blue, yellow silk and worked in coloured coils

Figure 1: The tarnished metal decorations and dusty skin of the Gloves of Charles I (at Ripley's museum, London, UK).

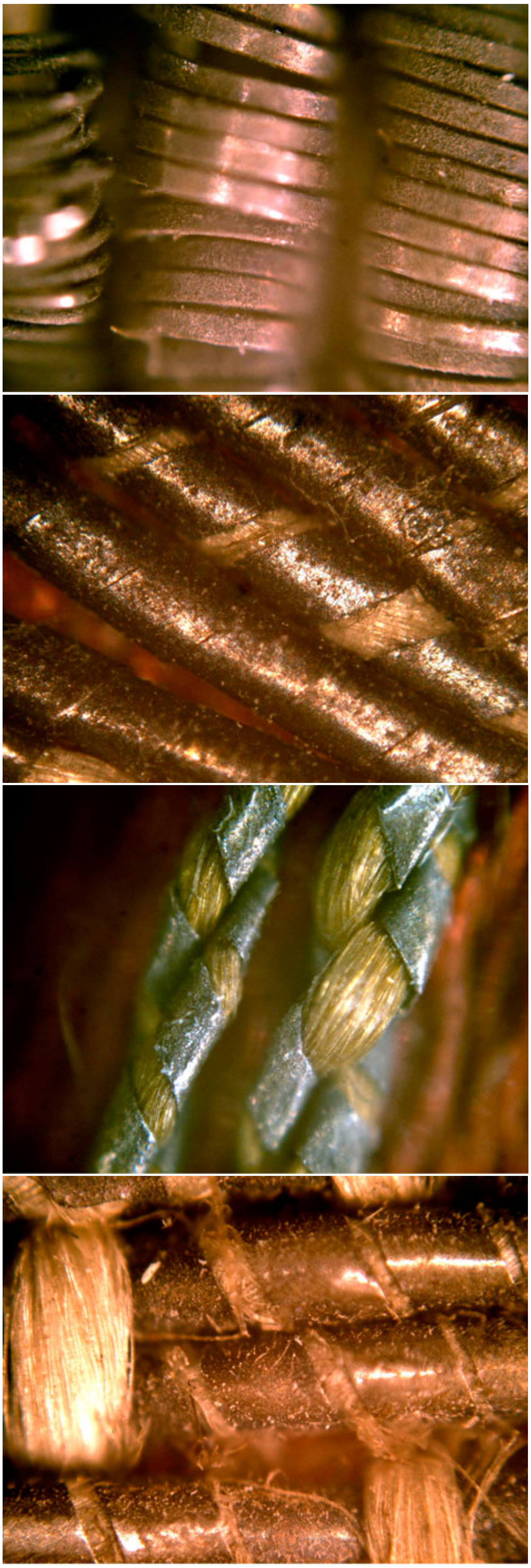

Figure 2: Show different designs of the tarnish of gilt-silver threads.

of metal thread, together with leaves and a curios bird-like dragon formed by strips of metal coils. Due to the atmospheric pollution, the metal threads have been corroded and covered by black-tarnished crystals of corrosion products and dirt, which compromise the legibility of the decorative design by forming dark fur-like growth. Furthermore, loose metal threads have been collected and fungal infection was recorded on the leather. Laser cleaning tests were performed on some separated metal strips.

2.2 Lasers

Laser cleaning tests were performed using the High Q custom Nd:Van regenerative amplifier picosecond laser (Figure 3) with a repetition rate of 10 kHz with output wavelengths of 1064 nm and a temporal pulse length of 10 ps (FWHM). The picosecond laser tests were carried out using scanning laser with fluences regulated between 0.62- 6 J cm^{-2}, power output 100 mW; number of scans 5-20, traverse speed 300-825 mm s^{-1}; laser spot size: 30 µm (constant); Hatch spacing: 0.03 mm (constant) and 10 kHz repetition rate. The lasers were clamped at a fixed position above the sample, which was mounted on A3-axis motion control system (Aerotech) in conjunction with NView MMI software to manipulate samples and select the size of scanning area with automatic distance detection and adjustment of the laser focus. The experimental set up of the ultrafast laser systems employed here has been reported for conservation purposes elsewhere.[16-18]

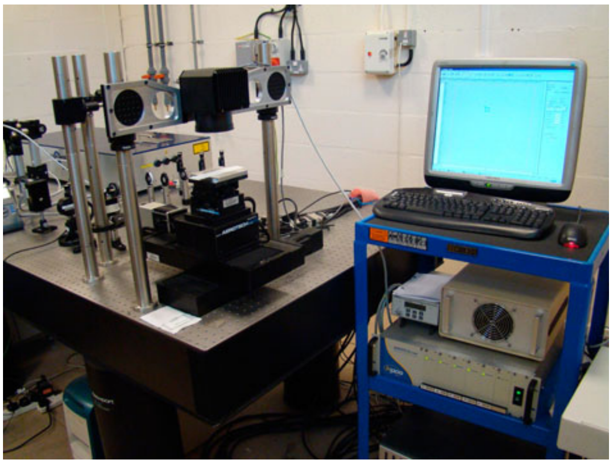

Figure 3: Show the High Q custom Nd:Van regenerative amplifier picosecond system.

2.3 Analytical instrumentation

For the elemental analysis of the deterioration products and assessment of laser tests, a Scanning electron microscope (Carl Zeiss Ultra Plus Field Emission) connected with energy dispersive X-ray (EDX) detector (Oxford instruments X-Max) has been employed. The instrument has ultra high-resolution secondary and backscatter electron imaging (1 nm) utilising a new in-lens detector technology. Further, there is a charge compensation system for the imaging of non-conducting samples. Olympus model optical microscope with a maximum magnification of 40× was used to investigate damage signs and assess laser cleaning tests.

Raman spectroscopy has been carried out for the technical analysis of the gloves material. Raman analysis was carried out using a Renishaw RM2000 single grating (1200 mm^{-1}) spectrometer coupled to an optical microscope and to a 578 × 400 pixels air-cooled CCD detector was used for micro-Raman analysis. A solid-state diode laser emitting at 785 nm was employed for analysis. In this configuration, a spectral resolution of 4 cm^{-1} was focused on the sample using a 50X objective (N. A. 0. 7), which provided a spatial resolution of approximately 5 µm The grating calibration was evaluated on a silicon wafer by checking the Raman band at 520 cm^{-1}. Acquisition times ranged from 100 to 300 sec. As the textile sample was very fluorescent; a Raman spectrum has been obtained by applying a baseline subtraction in order to partially remove contributions from luminescence.

3 Results and discussion

3.1 Technical analysis and damage assessment

The construction of the metal threads of the gloves in the middle ages in Great Britain is varied and many techniques were employed.[19,20] The use of more than one technique within the same textile is entirely possible.[21] A single textile may have both gold and silver threads, S and Z twisted wrapping or both woven flat strips and wrapped strips where the strips have been beaten and cut or it has been cast, drawn and rolled. The microscopic investigations of the selected gloves show the employment of different type of metal threads (round and flattened). These metal threads were distinguished by the weave and embroidery patterns with the use of ~30 um-70 um strip width.[14,22] SEM-EDX analysis of the metal threads indicates the presence of silver and the gold elements with a presence of copper as a part of the original alloy. Furthermore, the results indicate the employment of pure silver threads and gilt-silver threads. (Figure 4). Micro Raman spectra were acquired from extracted dyed fibres from the decorated gloves. The sample was very luminescent and therefore, in order to extract legible Raman bands, a baseline subtraction and spectral smoothing were applied. Although the noise is quite high, corrected Raman spectra indicate that the fibre is silk dyed with a carmine-based lake (cochineal or kermes, Figure 5). Bands at 850 cm^{-1}, 990 cm^{-1}, 1090 cm^{-1}, 1245 cm^{-1}, 1450 cm^{-1} and 1660 cm^{-1} are attributed to silk.[23] The red carmine dye is associated with bands at 1315 cm^{-1}, 1410 cm^{-1}, 1600 cm^{-1}, characteristic vibrations of the complex formed between anthraquinone-aluminium ions.[24] Unfortunately, the extraction of the dye from the tissue could not be perform in order to

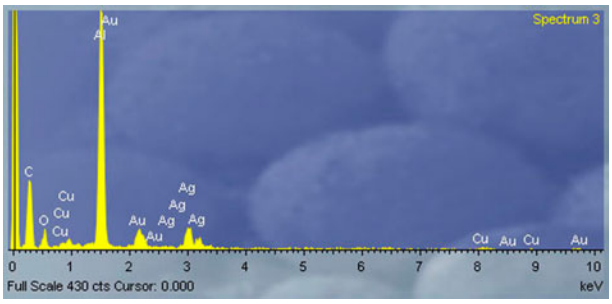

Figure 4: Show SEM-EDX analysis of the metal threads indicates the presence of gold with a presence of silver and copper as a part of the original alloy.

carry out SERS spectroscopy measurements to enhance the pigment Raman signal because the same sample (a few μg) was used for multiple analysis using different non-destructive techniques. SEM-EDX imaging analysis of the tarnish over the metal threads indicated the presence of corrosion products of silver sulphide and silver chloride while dirt components (Sodium aluminium silicates) were also detected (Figure 6, 7).

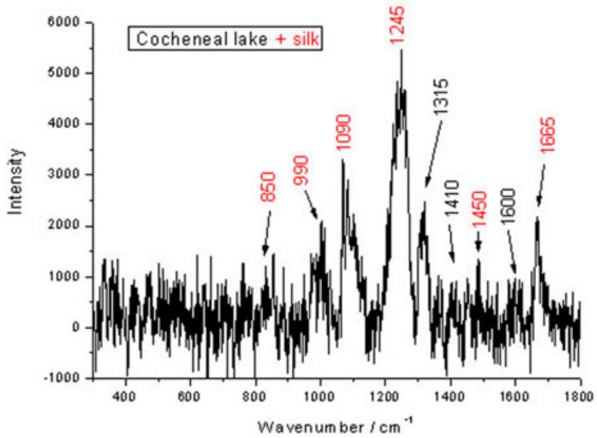

Figure 5: Micro Raman spectra of dyed textile of gloves. Raman spectra indicate that the fibre is silk dyed with a carmine-based lake.

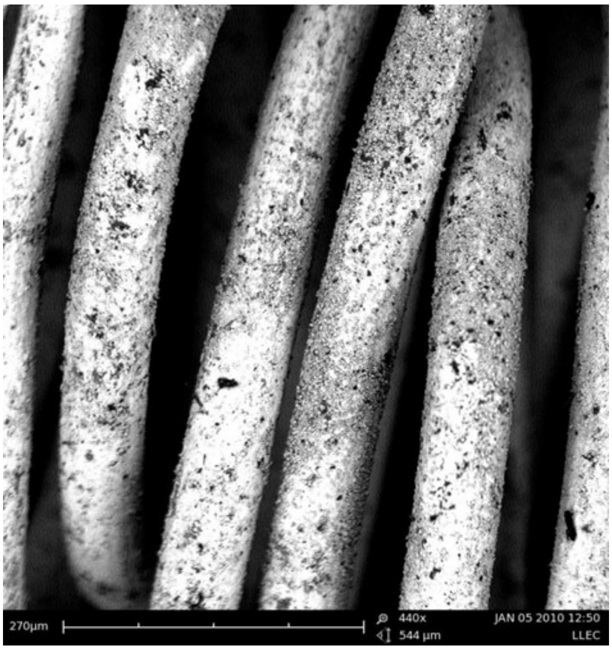

Figure 6: SEM imaging of the tarnish and contamination over the round metal threads of the gloves.

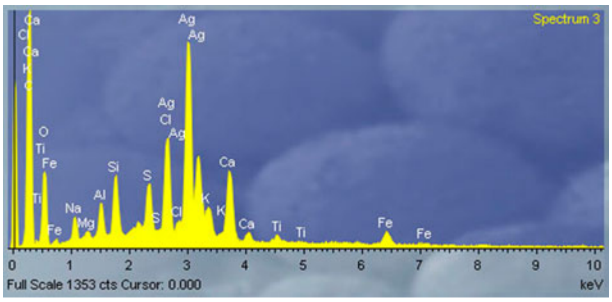

Figure 7: SEM-EDX analysis of the tarnish over the metal threads indicated the presence of corrosion products of silver sulphide and silver chloride with dirt components (Sodium Aluminium Silicates).

3.2 Laser cleaning tests

Optimization of the laser cleaning parameters was performed for determination of damage/ablation threshold fluences of each substrate and optimal focus point sizes and laser intensities. This requires an intensive investigation and selection of various laser parameters to assess the cleaning of the gloves with its different components. For removal of the tarnish layers from the silver or gilt-silver threads, scanning picosecond laser cleaning tests were performed in a high speed of uniform horizontal square/rectangular laser scanning using various numbers of scans and fluences on seperated metal strips. Lasers have been focused on the threads surfaces to have a controlled surface ablation of small amounts of contamination and from crevices and pits which are difficult to access by traditional cleaning methods. Future irradiation of the fibre core or the dyed textile ground, which is sensitive to light,[25] could be limited by selecting the cleaning areas and focusing the laser beam on the metal strips. The laser scanning area was adjusted on the basis of the shape and the dimensions of the surface area being cleaned under automated PC-driven scanning.

Microscopic investigation were performed to determine the damage threshold fluence of the selected loose metal threads in order to clean the metallic surface of the strips without potentially inducing damage (such as discoloring/pitting/removal of patina). Investigations indicated that ps laser irradiation could be used to remove the tarnish layer completely from metal threads at fluences of 1.91 J cm^{-2}, 5 scans, spot size of 30 microns, 300 $mm.s^{-1}$ traverse speed and hatch spacing of 0.03 mm (Figure 8). At the ablation threshold fluence, laser ablation satisfactory removed all of the tarnish without damage (whitening/melting) of the metal threads surfaces (Figure 9). The EDX analysis documented mainly the absence of tarnish elements (Sulpher and Chorine) for all treated layers after laser cleaning (Figure 10). With higher fluences and number of scans, melting or whiting or pitting of the threads surface could be observed (Figure 11). The

Figure 8: SEM imaging of satisfactory laser cleaning of tarnish from flattened surface of the metal threads at fluences of 1.91.

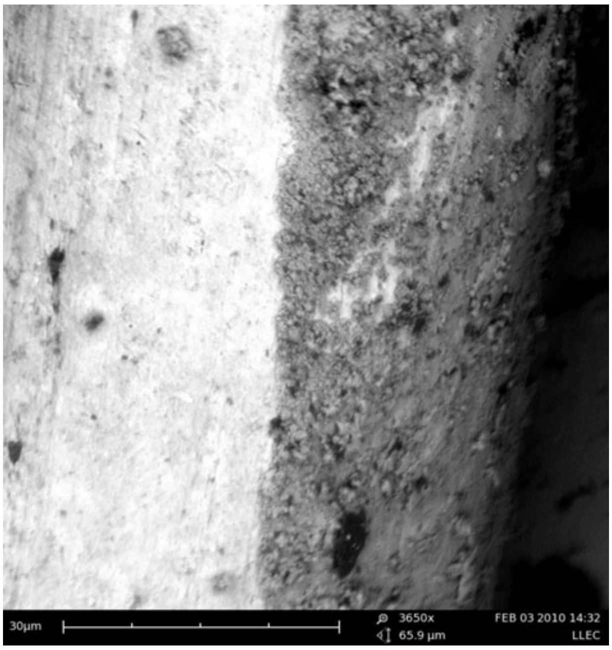

Figure 9: SEM imaging of satisfactory laser cleaning of tarnish from metal threads at fluences of 1.91 Jcm^{-2}, 5 scans, spot size of 30 microns, 300 $mm.s^{-1}$ traverse speed and hatch spacing of 0.03 mm (the left part of the of metal strip is laser cleaned and the right is non-cleaned).

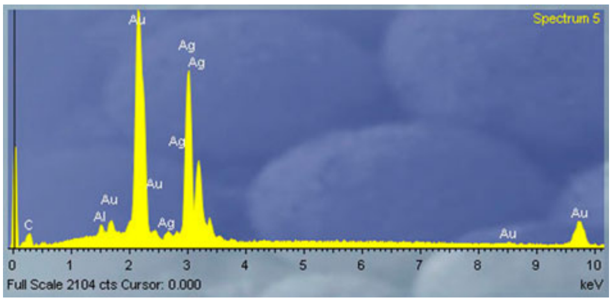

Figure 10: Show the EDX analysis of laser cleaned metal strip at fluences of 1.91 Jcm^{-2}, 5 scans with absence of tarnish ions (Sulpher and Chorine) and detection of gold and silver ions of the metal alloy.

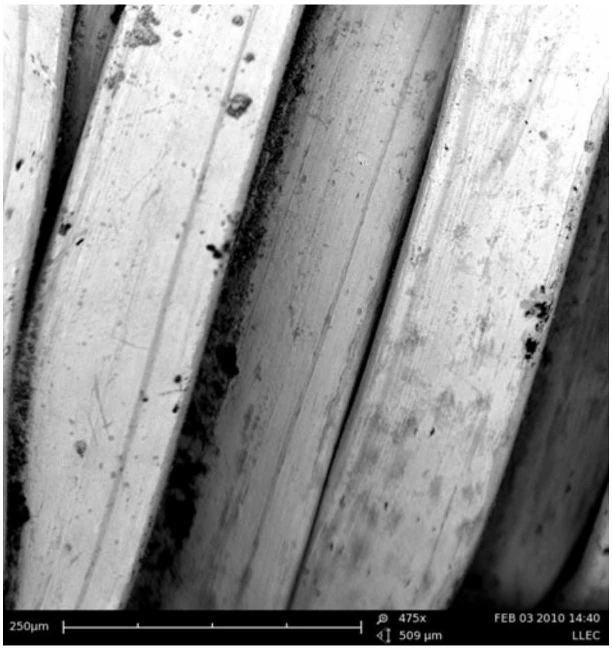

Figure 11: Show melting of the metal threads using irradiated at fluence of 2.5 Jcm^{-2} with 12 scans.

microscopic investigation of the irradiated metal strips shows that the damage threshold starts at fluence of 2.5 Jcm^{-2} with 5 scans. While similar damage aspects could be detected with using same ablation threshold fluence but with higher number of scans (12 scans). However, the curved and inaccessible areas of the metal strips could not be homogenously and completely treated without damaging the top surfaces. After cleaning of the silver and gilt-silver threads; the bright surfaces of the decorative metal threads has been revealed with improving the authentic and aesthetic appearance of the gloves.

4 Conclusion

Analytical study of the substrate and the unwanted materials was carried out for better understanding of the object materials, technology used and the deterioration phenomena. The assessment of ultrashort ps laser for satisfactory cleaning of metal strips was enhanced by microscopy and X-ray energy dispersive spectroscopy. While ultrashort pulse duration of the ps laser system used led to micro size scales of material ablated on the metal strips, which provided a high precise and ultra-gentle cleaning, future fast scanning of the laser pulses could allow expansion of ps laser cleaning of dirt over large areas of the gloves in short time. The promising results of the work addressed here using ultrafast ps laser recommend the need of developing new mobiles systems for conservation needs with more applications on heritage material for better assessment of the new system. One of the disadvantages, beside the shortage of commercial availability and high cost, for the employment of ultrashort lasers for cleaning of artworks is the large size of laser unit which limit the mobility of the laser cleaning system. Furthermore, the object surface needs to be kept flat as much as possible to maintain the constant laser parameters and the homogeneity of the cleaning results.

5 Acknowledgements

Micro-Raman measurements were carried out at the Chemistry Department of the University Of Florence. The author thanks Yvette Fletcher from leather conservation centre (Northampton, UK) for helping with object diagnosis.

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