The Use of an Er:YAG Laser in the Removal of Biological Growth from Polychrome Archaeological Terracotta Figurines from Cyprus

ABSTRACT

The British Museum preserves a large and archaeologically important collection of painted terracotta and limestone figurines from ancient Cyprus. These were the subject of a collaborative conservation and study programme as part of the Cyprus Digitisation Project. The figurines were covered by dark and ingrained speckles of biological growth, possibly linked to inappropriate storage conditions in the museum. These speckles significantly disfigured the appearance of the figurines and obscured physical features, manufacturing details, and surviving pigments. Traditional conservation treatment methods proved ineffective in reducing or removing the dark speckles on the terracottas, leading to the consideration of the use of an erbium yttrium aluminum garnet (Er:YAG) laser, since this technique proved successful in cleaning biological growth from the polychrome limestone figurines in the same collection. This study comprises the first known use of this technology on polychrome terracotta affected by biological growth. Highly satisfactory results were achieved, improving the understanding of archaeological aspects of the objects, while also pushing forward conservation science.

KEYWORDS

Er:YAG lasers · Cleaning · Biological growth · Mould · Terracotta · Limestone · Polychromy · Archaeology

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BACKGROUND OF THE PROJECT

The British Museum (BM) holds one of the largest and archaeologically most important collections of terracotta and limestone statues and figurines from Cyprus outside the island itself. The figures range in date from the Bronze Age to Roman times, but are predominantly from the Cypro-Archaic and Cypro-Classical periods (ca. 750 BCE-300 BCE), with some later Hellenistic and Roman examples (ca. 300 BCE-200 CE). The large majority were excavated or collected during the 19th century by amateur archaeologists and later by scientific bodies such as the Cyprus Exploration Fund and the BM, and were sent to different academic institutions in Britain, including the BM, the Ashmolean, and Fitzwilliam Museum.

Most of the terracotta and limestone figures in the BM derive from sanctuary sites and tombs where they were offered as gifts to the gods or to the deceased. Examples have also been found in

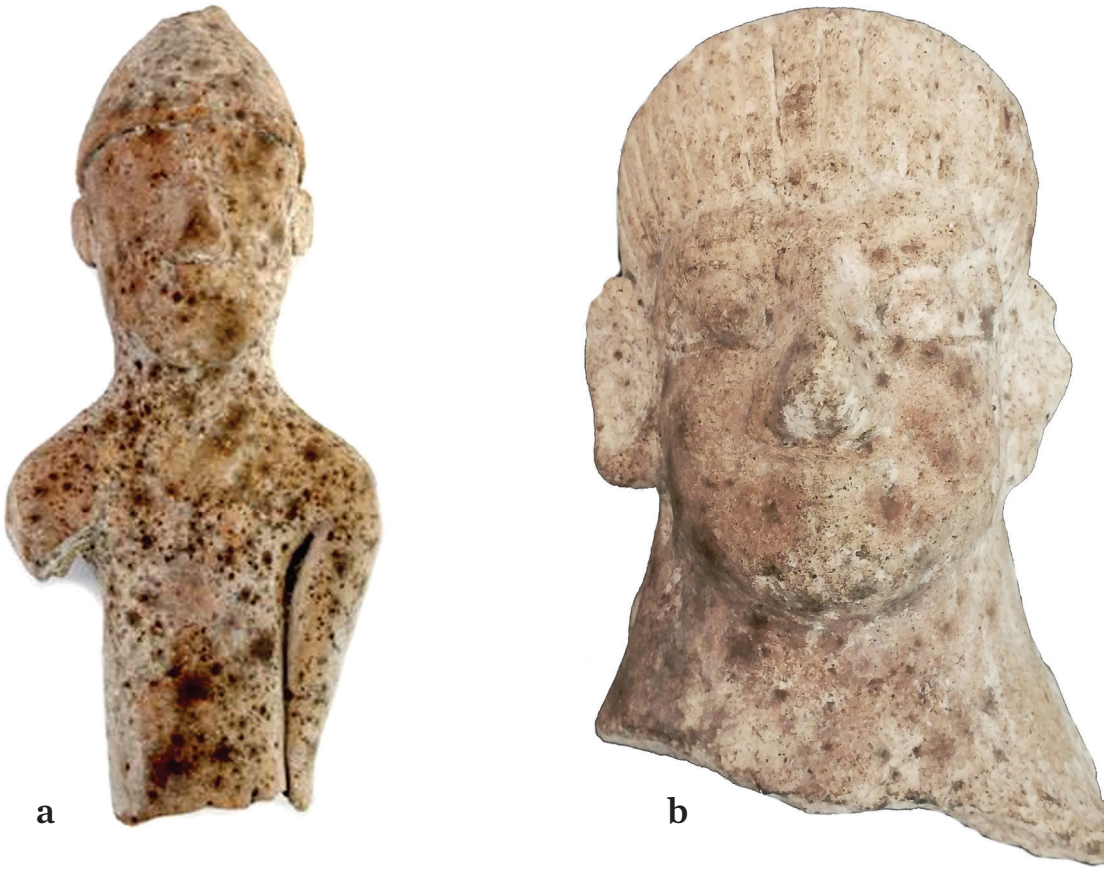

Figure 1. *Stained figurines*
a) 7th-6th century BCE, Cypro-Archaic, terracotta, H 17.5 cm × W 8 cm. British Museum, 1873,0320.136;
b) 7th-6th century BCE, Cypro-Archaic, terracotta, H 11 cm × W 7.5 cm. British Museum, 1873,0320.148 ·
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settlements and even in shipwrecks, as well as other maritime contexts. The figurines represent animal and human figures, male and female, as well as inanimate objects, such as boats and carts, sometimes showing a high level of detail in the clothing and jewellery (Karageorghis and Karageorghis 1991-1999). According to their function, they vary in size from larger than life-size display pieces to very small and intimate items. Some were richly coloured, although the original painted decoration has, in many cases, partly or completely disappeared due to a range of post-depositional conditions.

The figurines in the BM have been extensively studied from the point of view of religious iconography and artistic traditions, though far less work has been undertaken on technical aspects such as clay sources, manufacturing methods, and polychromy. As part of the BM's Cyprus Digitisation Project, the figurines have become the subject of intensive research. The project aims to create a comprehensive online catalogue of this collection, facilitating their study, photography, and display in the Museum and online, guaranteeing long-term care, future research, and public access.

The study of this collection is made difficult by the extensive surface staining affecting a large proportion of figurines, which obscures features and remnants of polychromy. Therefore, a multidisciplinary team consisting of a curator, conservators, and scientists began to investigate both the origin of the staining problem and treatment options for the limestone and terracotta figurines. This paper will focus on the treatment of the terracotta figurines. Initial observations under magnification determined that the staining was biological in nature; and, to better understand the precise issue, the team conducted a thorough investigation into the history of the figurines in order to identify when, where, and how the condition arose.

Figure 2. *Figurine a) with ingrained speckles on the front and b) no speckles on the back. 7th-6th century BCE, Cypro-Archaic, terracotta, H 19.5 cm × W 4.5 cm. British Museum, 1873,0320.144 · Copyright of the Trustees of the British Museum*

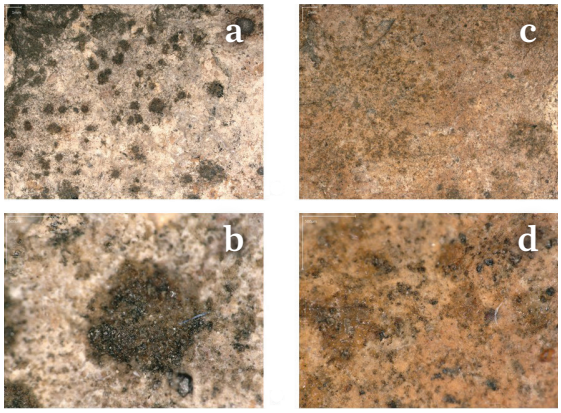

Figure 3. *Micro-photographs of figurines showing examples of a, b) thicker speckles, 7th-6th century BCE, Cypro-Archaic, terracotta, H 17 cm × W 6.4 cm. British Museum, 1967,1103.17 and c, d) thinner speckles, 7th-6th century BCE, Cypro-Archaic, terracotta, H 17.5 cm × W 4.5 cm. British Museum, 1967,1104.10*

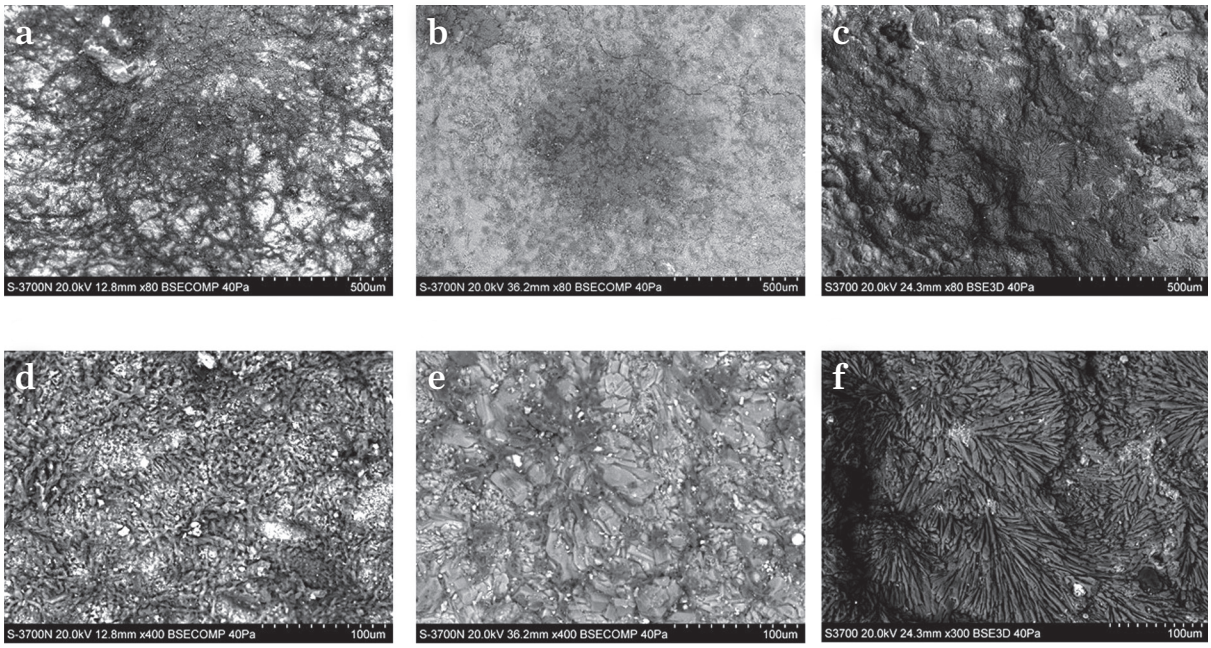

Figure 4. *Appearance of biological growth under SEM-EDX · Copyright of the Trustees of the British Museum*

PRELIMINARY RESEARCH

Conservation problem: Description and causes

At least half of the Cypro-Archaic terracotta collection is affected by the staining, amounting to more than 80 objects identified so far, of which 24 retain pigments (Figure 1). Macroscopic examination of the figurines showed that, in many cases, the reddish-brown speckles covered a large proportion of their surfaces and that, in general, the backs of almost all the figurines were free from speckles. This suggests that the way the collection was stored, with the figurines lying on their backs, and the microclimate in the storage area played a role in the organism's spread (Figure 2).

Observations under the microscope revealed that, in some instances, the staining appeared thinner and more superficial, while in others it was thicker and more ingrained (Figure 3). Upon initial inspection, the staining resembled an old mould colonisation, although manganese oxide staining, which is sometimes found on archaeological ceramics (Costello et al. 2018),

could not be excluded. Therefore, the figurines were further investigated non-invasively using scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDX). The stains' morphologies at high magnification, up to 500x, were relatively varied (Figure 4), ranging from networks of filaments to star-shaped formations. The EDX elemental analysis of the speckles showed high carbon content and no manganese or iron, thus excluding manganese dioxide staining and confirming past biological growth as the most likely cause of the staining. The biological growth currently appears inactive, as the organisms look dry, both to the naked eye and under high magnification. Moreover, archival images from the 1980s show that the pattern of the speckles was already present and remains unchanged.

Biological colonisation of ceramics is a known phenomenon, more frequently found in outdoor environments, such as on tiles and other architectural elements (Coutinho, Miller, and Macedo 2015), and far less common in museums. However, archaeological ceramics in museums can carry fungal spores from the burial environment which, in favourable ambient conditions such as high humidity, can germinate and eventually cause an outbreak. Roughness and high porosity make ceramics more bio-receptive; and, during investigation, it became evident that the Cypro-Archaic figurines, fired at lower temperatures and therefore with very porous fabrics, have been affected more severely than the Hellenistic examples with finer and less porous fabrics. Organic nutrients on the objects, whether from soil or accumulated dirt, can also contribute to sustaining microbial life. However, the presence of photosynthetic organisms, which do not require organic matter as a source of nutrients, could not be ruled out. A lichenised fungus is the most likely coloniser in this case; however, the distortion of the features of the dry organisms under the microscope complicates an accurate identification.

Research into the history of the collection within and outside the museum suggests that the outbreak most likely happened after the objects arrived at the BM. This is supported by three points. Firstly, figurines from the same 19th century excavations held in other UK museums do not show any evidence of staining. Secondly, the wooden and stone mounts, which were later additions to the objects once at the BM, also show signs of staining. Finally, more ceramic objects from other collections in the Museum were found to bear the same kind of spotting, implying that all of these objects might have been stored together when the outbreak occurred.

Conversations with curators, collection managers, and conservators, and consultation of historical photographs revealed that the collection was kept in unsuitable and uncontrolled conditions in the 19th and 20th centuries before the development of modern museum conservation. Archival records from this time show that the figurines were moved between various locations, possibly due to storage flooding and consequent issues of dampness, but also in response to more general changes in display and storage strategies. In the early 2000s, the figurines were moved into a refurbished storage space with a controlled environment, where they are kept inside metal drawers lined with inert Plastazote foam.

Evaluation of treatment options

Assessment of the figurines highlighted several challenges limiting treatment options:

- the presence of vulnerable polychromy hidden beneath the speckles;
- the stubbornness and depth of penetration of the biological growth combined with the porous and delicate nature of the substrate, makes the figurines prone to staining, softening, and mechanical damage during treatment; and
- the large number of figurines affected and the consequent additional time required for treatment.

Dry, ingrained biological growth is very different from the fresh and active kind, normally removed through brush-vacuuming and swabbing with solvents. Old growth of this kind is rarely found in a museum context and, so far, no conservation methods have been developed to remove it at the BM. Chemical cleaning and biocide treatments used on outdoor architectural ceramic substrates, such as tiles, were immediately discarded as unsuitable. All conventional cleaning methods tested, which included deionised water, acetone, and agar gel, produced unsatisfactory results and only slightly reduced the size of the speckles. In addition, these cleaning systems could be applied only to the unpainted figurines. Any further

Figure 5. *Er:YAG laser at the BM during treatment · Copyright of the Trustees of the British Museum*

swabbing or poultice applications resulted in an over-cleaned patch around the speckles and abrasion of the surface.

This underlined the need to explore an alternative method, which would be time-efficient, controllable, and selective. Modern lasers possess these characteristics and have proved successful in removing biological growth from a variety of substrates, particularly stone (De Cruz et al. 2005).

The successful laser cleaning of polychrome limestone figurines from the same Cypriot collection prompted the team to consider its use to treat the terracotta figurines. The more widespread Q-switched neodymium yttrium aluminum garnet (QS-Nd:YAG) laser (1064 nm and 532 nm) was useful in removing the staining from the limestone, but could only be used in the absence of pigment. A recently donated Er:YAG laser was the method of choice for the painted areas (Figure 5). On the terracotta figurines, preliminary testing with the Nd:YAG laser on discrete areas resulted in discolouration and overcleaning. These observations led to choosing the Er:YAG lasers for the treatment of both painted and unpainted figurines. There appears to be no documented research on the effectiveness of Er:YAG lasers in the removal of biological growth from terracotta, but the unique characteristics of this type of laser make it well suited for this task:

- Er:YAG lasers emit radiation at 2940 nm, a wavelength readily absorbed by hydroxyl groups (-OH). Biological growth would be sensitive to this type of laser, as confirmed by De Cruz et al. (2009), who successfully removed lichens from limestone using Er:YAG lasers.
- The action of Er:YAG lasers is confined to the top layer of the irradiated surface; the penetration of the laser is only a few microns per laser pass. This allows for a very controlled cleaning, where unwanted material is gradually thinned (Pereira-Pardo and Korenberg 2018).
- In general, painted surfaces are stable to Er:YAG laser treatment. The reflectance of 2940 nm radiation of many pigments has been the subject of various studies and the damage thresholds of many pigments have been published (Pereira-Pardo and Korenberg 2018).

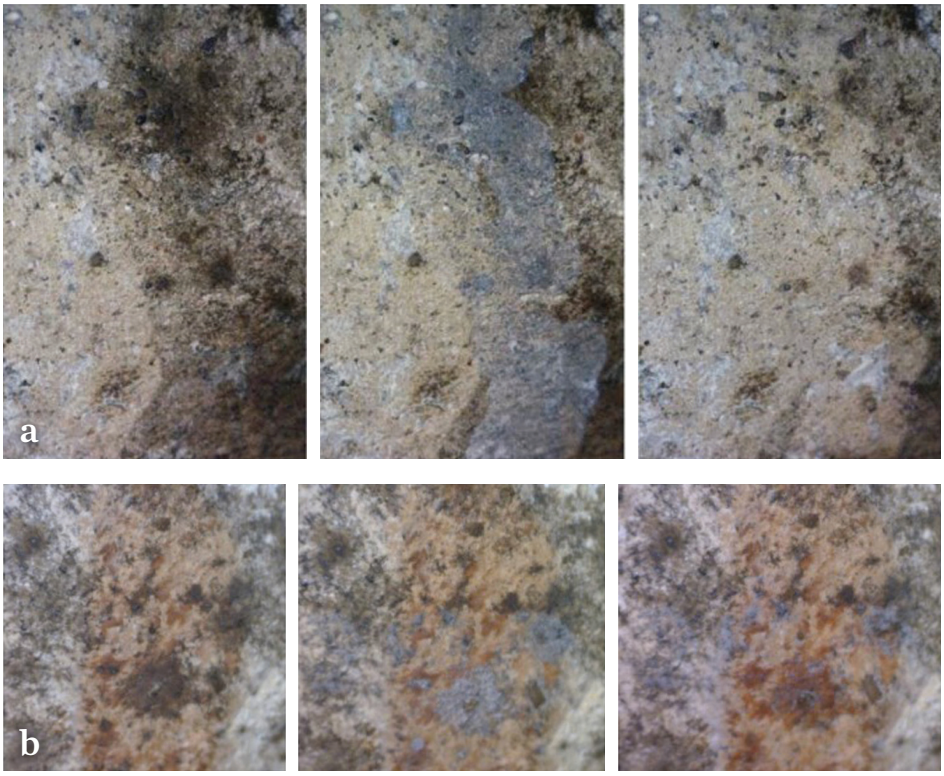

Figure 6. *Micro-photographs of a) unpainted (1873, 0320.136) and b) painted (1873, 0320.153) figurines showing biological growth before cleaning (left), after laser irradiation (center), and after gentle swabbing (right)* · *Copyright of the Trustees of the British Museum*

- The laser spot size can be fixed so it does not vary with the working distance. This allows for a safe and even cleaning of 3D objects.
- Optimal results are achieved in combination with traditional cleaning methods, such as swabbing after irradiation.

Scientific analysis of the figurines' materials

Before proceeding with the Er:YAG laser treatment, the figurines were analysed by multiple techniques in order to characterise the terracotta substrate and the pigments and determine their sensitivity to the laser radiation (Table 1 and Experimental). A relatively limited palette was detected, which included red and yellow ochre, manganese black, green earth, and traces of Egyptian blue. The materials identified are consistent with those documented in the literature on Ancient Cypriot sculpture (Gasanova et al. 2017).

After identification, the sensitivity of the materials to laser radiation at 2940 nm was assessed. Whenever available, published damage thresholds were consulted (Bracco et al. 2001). Additionally, experimental laser tests on mock-up samples of green earth and Egyptian blue were performed in order to determine the level of energy that would cause any change in the material. Safe irradiation conditions were established for the pigments that were more susceptible to degradation under laser irradiation, such as yellow ochre and green earth. Therefore, irradiation was avoided, or a lower fluence used, in their presence.

LASER TREATMENT AND EVALUATION OF THE LASER EFFECTS

Four Cypro-Archaic figurines were selected for the initial laser trials, including the two painted examples in Figure 1. A discrete area of the figurines was selected to be irradiated, in order to assess how the speckles responded to different values of fluence. They were irradiated both in dry and wet conditions, applying a small amount of either deionised water or isopropanol before the laser pulse, as using a wetting agent

MATERIALS	DESCRIPTION	COMPOSITION	ANALYTICAL TECHNIQUES	SENSITIVE TO Er:YAG?
Ceramic substrate	Hard and red-brick colour or softer and yellowish	Major: Si, Al; Minor: Mg, Fe, Ti, K, Na; Traces: Pb	SEM-EDX	No
Burial crust	White, discontinuous, friable, thin veil or thick crust	Calcareous: calcite, gypsum	SEM-EDX, FTIR, Raman	Yes
Pigments	Red	Hematite	SEM-EDX, Raman	No
	Yellow	Iron-based yellow (likely goethite)	XRF, OM	Yes
	Black	Manganese oxide	SEM-EDX, XRF	No
	Green	Green earth	FTIR	Yes
	Blue (traces)	Egyptian blue	MSI-VIL, Raman	No
	Flesh tones (pink)	Iron-based red (likely hematite)	XRF, OM	No

Table 1. *Characterisation of the materials present in the terracotta figurines selected for Er:YAG treatment*

increases the efficiency of the laser by adding hydroxyl groups and protects the surface by dissipating heat (Pereira-Pardo and Korenberg 2018). Results were very promising, as shown in the micro-photographs in Figure 6. A reduction of the staining was observed after a single pulse at low fluence, below 1.5 J/cm^2, in both wet and dry conditions. Slightly higher fluences or more laser passes were needed for more stubborn speckles. Erbium lasers work best in combination with other methods (DeCruz et al. 2009); in this treatment, swabbing with 1:1 deionised water:acetone after laser irradiation was found to efficiently remove any debris without staining the surface.

Following preliminary trials, optimal parameters for the treatment of the terracotta figurines were determined: irradiating dry or after application of a thin layer of deionised water for more stubborn speckles; with energy of 70 mJ and laser spot size of 2.1 mm in diameter for a fluence of 2.0 J/cm^2; and pulse duration of 100 µs. Residues were swabbed with a 1:1 mixture of acetone and deionised water.

The effects of the irradiation on the substrate were carefully assessed by means of optical microscopy, colour measurements, and SEM-EDX. The area at the back of the figurines that was not affected by biological growth and, therefore, not treated using the laser, was used as a reference to compare with the laser-cleaned areas. No surface change was observed under high magnification up to 500x, even on the polychrome areas. Colour measurements taken from the cleaned areas showed no relative colour change when compared to reference areas: ΔE_{76} 2.5, Δa 0.1, Δb 0.5, ΔL 2.9. Finally, no changes in surface texture or composition were observed with SEM-EDX.

Regarding the effectiveness of the treatment, the laser successfully removed the staining and reduced remnants of vegetative growth (Figure 7). Colour measurements before and after laser cleaning also revealed that the CIELab components shifted towards the colour of the back of the figurines, unaffected by the staining. Finally, the laser treatment was extremely time-efficient, requiring only one to two hours of work per figurine.

Figure 7. *Terracotta figurines after laser treatment: a) 1873,0320.136, b) 1873,0320.148 · Copyright of the Trustees of the British Museum*

CONCLUSIONS

The characteristics of Er:YAG lasers allowed for the safe and efficient removal of the biological staining at low fluence values, not exceeding 2 J/cm^2, thus overcoming the conservation challenges posed by the presence of stubborn speckles on the delicate polychrome surfaces of the figurines.

As a result of the treatment, new light was shed on this important collection. Apart from revealing previously obscured features and painted decoration, this project has elucidated aspects of fabric, manufacturing, use of colour, and the impact of post-depositional conditions on the present state of the objects. In turn, this facilitates the study, photography, and display of the collection.

This work shows the success of interdepartmental and interdisciplinary collaboration in the conservation, scientific, and curatorial context. The project allowed for a better understanding of the material in both technical and cultural terms, and highlighted the importance of how the knowledge of past collection care can better inform current practices.

This project comprises the first known use of Er:YAG lasers for the cleaning of biological growth from polychrome terracottas. This research demonstrates great potential for the treatment of objects where traditional cleaning methods are inadequate or unsuccessful, or might harm original elements of the decoration such as paint or surface treatments.

EXPERIMENTAL

Laser

A Fidelis XS erbium yttrium aluminum garnet laser (Er:YAG) by Fotona emitting at 2940 nm was used for the cleaning tests and treatment of the terracotta figurines. The pulse width was set to 100 μs and the laser spot size, as measured on thermal paper, was 2.1 mm in diameter. The energy range used for the preliminary tests was 40-70 mJ, yielding a fluence between 1.2 and 2.0 J/cm^2. Frequency was kept at 3 Hz or 4 Hz.

Microscopy

A Dino Lite and a Keyence VHX-5000 digital microscope were used to record magnified images of the objects at 20× to 200× and assess their surfaces before and after the laser treatment.

Fibre optics reflectance spectroscopy (FORS) and colorimetry

An AvaSpec-ULS2048XL-USB2 fibre optic spectrometer by Avantes was used, equipped with a 2048 pixel CCD linear array detector and an AvaLight-HAL-S-IND tungsten halogen light source. The probe was set at approximately 45° from the surface normal to exclude specular reflectance. The spectral range considered was from 300 nm to 800 nm. The best spectral resolution was 2.4 nm calculated as full width half maximum (FWHM). Spectra were referenced against a white WS-2 tile from Avantes, 92-98 percent reflectance. The diameter of the investigated area was approximately 2 mm. The integration time was 100 ms, and each spectrum was the average of three acquisitions. The CIELab colour coordinates were determined before and after laser treatment and the colour difference was calculated applying the Delta E_{76} formula. The whole system was managed by the software AvaSoft 8 for Windows.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy was performed on a Nicolet 6700 spectrometer attached to a Continuum IR microscope equipped with MCT/A detectors. Samples were analysed in transmission mode, flattened in a diamond micro-compression cell. The field of view was controlled by the sliding aperture, with a maximum area of analysis of 100 μm × 100 μm. The spectra were acquired over a range of 4000-650 cm^{-1} using 64 scans at a resolution of 4 cm^{-1} and automatic gain.

Variable pressure scanning electron microscopy with energy dispersive X-ray spectrometry (VP-SEM-EDX)

A Hitachi S3700 VP-SEM was used in low vacuum mode, operating at 20 kV, to investigate the surface of the objects in detail and to do the elemental analysis of the pigment remnants. The EDX spectra were collected using an Oxford Instruments INCA EDX spectrometer with a 0-10 KeV spectral range and 150 seconds live time. Quantitative analysis was calibrated using a cobalt standard and Oxford instruments INCA software.

Multispectral imaging (MSI)

The figurines were photographed with a modified Canon 40D camera body, where the inbuilt UV-IR blocking filter was removed to exploit the full sensitivity of the CMOS sensor, approximately 300–1000 nm. The lens used was a Canon EF 50mm f/1.8II. Visible-induced infrared luminescence (VIL) imaging was used to identify Egyptian blue, using high power LED light sources (R 630 nm, G 520 nm,) and a Schott RG830 cut-on filter, 50 percent transmittance at 830 nm. A reference grey scale and a Macbeth ColorChecker were placed next to the objects. Images were acquired as raw files and transformed into 3888 × 2592 pixel resolution images in 16-bit TIF format. Standardisation and calibration of the images were then carried out using 'BM_workspace', a plug-in for Nip2-VIPS.

Raman spectroscopy

Raman spectroscopy was carried out with a Jobin Yvon LabRam Infinity spectrometer using a green 532 nm laser with maximum power of 2.4 mW at the sample, a liquid nitrogen cooled CCD detector, and an Olympus microscope system. Small figurines were analysed non-invasively by placing them under the microscope objective, 50-100×, and focusing the laser on the pigment particles. When this was not possible, samples of a few grains were collected using a clean scalpel, placed onto a microscope slide, and measured without any further treatment. The resultant spectra were identified by comparison with a British Museum in-house database and published literature (Bell, Clark, and Gibbs 1997; Burgio and Clark 2001).

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