Raman Spectroscopy Interrogating Historic Painted Textiles

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INTRODUCTION
Raman spectroscopy has been widely applied for archaeometric analysis since its first reported use [1]. It now finds increasing application in the worlds of art and archaeology [1-5]. Specific examples of recently reported applications include the analysis of pigments in fine art [6], wall paintings [7], wall coverings [8], polychromes [9], icons [10] papyri and manuscripts [11-19], the study of varnishes and binding materials [20], the analysis of pigments in glazes on pottery [21], and on Egyptian faience [22] and for analysing ceramic materials themselves [23-26], the identification of dyes on papers [27] and dyes on textiles [28]. Studies have also been undertaken on organic remains including the ‘ice man’ from the Alps [29] and skeletal remains [30]. Finally the technique has been used to identify the degradation and decomposition products on historic artifacts to inform conservation procedures [12,13,19]. Such analyses cross the boundary between science and the arts, offering new insight into the provenance of artifacts and clarifying cross-cultural influences. An excellent overview of this topic can be found in [31].

Conservators of historic painted textiles at the Textile Conservation Centre, Winchester, are exploring the potential of Raman spectroscopy in the analysis of pigments used, throughout history, on painted textiles such as trade union banners, religious and military colours, upholstery and furnishing fabrics, costumes for theatre and normal wear, tapestry cartoons and stained cloths (cheap imitations of tapestries) or even painted areas used to fill in missing areas of damaged tapestries. They seek knowledge of the original pigments to understand the appearance of an artifact, especially if fading has degraded the pigment, or to authenticate artifacts by identifying the presence of a synthetic pigment whose first date of manufacture is known. Whilst databases of pigments found on paintings exist, such information cannot necessarily be used directly in textile conservation as the pigments listed may have different significance or prominence.

Painted textiles differ from paintings in that only a part of the supporting fabric is painted and, not being stretched on a frame, it remains flexible. This flexing can result in severe damage to the painted areas. To determine the appropriate restoration or cleaning processes, textile conservators have to consider the nature of the pigments, the paint binder, any surface finish and the nature of any soiling. They also have to identify any non-original paint that may have been used as part of an earlier restoration process. Finally health and safety considerations dictate that conservators handling fragments from friable samples during conservation treatments must take appropriate precautions should artifacts contain toxic materials such as lead, arsenic and mercury as was common in early pigments.

Raman spectroscopy lends itself to the study of painted textiles in that: it generally requires no sample preparation; has the potential to be used directly in textile conservation as the pigments such information cannot necessarily be used; and, with the appropriate protocol, is non-destructive. This is essential as it is not considered ethical to remove part of a painted textile for testing, and the paint layer is often so thin that paint cannot be removed without damaging the fabric.

This study is the first of its kind to apply Raman spectroscopy to historic painted textiles. These, initially, appear to be non-ideal specimens for Raman spectroscopy for several reasons: organic materials, either incorporated into the binder or paint medium (typically egg yolk in the case of water colours and a drying oil such as linseed or walnut oil for oil paints) or used as a surface finish on textiles to achieve particular visual or protective effects (such as beeswax, blood or urine), will result in a large fluorescent background to the spec-
MATERIALS AND METHODS
The fabric sample used for this study was taken from the Karen Finch Reference Collection at the Textile Conservation Centre. It originally formed part of a painted silk chair cover, originating in China and recorded as belonging to the Doge Paolo Renier around 1750. It is considered to have been an exhibition piece to demonstrate the wealth of the owner rather than for everyday use. Small (typically 1 cm²) fabric samples exhibiting a range of colours were used, with no further sample preparation.

Preliminary microscopic analysis was undertaken with a Wild M3Z stereomicroscope with 1.0x objective and 10x eyepiece.

Initially, X-ray fluorescence (XRF) analysis of each coloured area was undertaken, using an EDAX Eagle II energy dispersive machine, to establish the main elements present. The instrument chamber has two digital cameras (x10 and x100) and the X-ray beam focuses to a spot of 0.3mm diameter.

Subsequent Raman spectroscopy of samples was performed using a Leica microscope coupled to a Renishaw Raman spectrometer with a 780 nm diode laser. A laser power of 25 mW was used at typically 25% or 10% power. The instrument has a Peltier-cooled charged-coupled device (CCD) detector and a holographic grating of 1800 grooves/mm. A holographic (notch) filter prevents backscattered (Rayleigh) radiation from entering the detector. A 50x microscope objective (NA 0.75) was used throughout and all spectra were processed using GRAMS/32 software.

RESULTS
Visual examination showed that there was a single paint layer with no ground (preparatory layer painted over the fabric before the paint is applied) or varnish (transparent resinous layer applied over the paint layer). This renders the pattern highly vulnerable for upholstery use and the paint surface appeared damaged as a result. The pigment appeared to be suspended in egg tempera (i.e. a watercolour rather than for everyday use. Small (typically 1 cm²) fabric samples exhibiting a range of colours were used, with no further sample preparation.

with paintings and manuscripts [32]. The prior use of XRF indicated the elements present and therefore helped identify possible pigments (Table 1).

Certain colour effects had been created by mixing pigments. Pale pink and pale blue were made from lead white mixed with vermilion and Prussian blue respectively. Darker shades of each colour were made by adding carbon black. Brown was created from mixtures of red lead and red ochre with Naples yellow added where a lighter; more orange shade was required. Purple was created by painting a layer of vermillion over carbon. The dark outlines to the flowers and leaves were carbon black (Fig 1 and 2). There was no Raman signal from uncoloured parts of the fabric thus no size or surface finish was detected.

DISCUSSION
Fluorescence was present in many of the spectra, despite the use of a long excitation wavelength (see Fig 3). However mineral-based pigments are sufficiently strong Raman scatterers that identifiable peaks were usually visible above the background fluorescence, allowing unambiguous identification of these pigments. Using the spectrometer in confocal mode reduced the fluorescence background but could not remove it entirely. Nonetheless the spectral quality was enhanced leading to easier identification of the pigments.

Studies of a selection of the pigments indi-
cated that photobleaching for several hours’ duration was also able to reduce background fluorescence. However, during this process, the relative heights of some of the peaks altered. This may indicate thermally induced damage to the pigments akin to the fading induced by exposure to visible or ultraviolet light. Extended exposure to laser light is not to be recommended for this reason. This signals caution when using lasers to clean historic artifacts: a technique that has been increasingly used in recent years.

The red flower (Fig 6) initially gave spectra indicating the presence of litharge (Fig 4). However, further work showed that this resulted from thermal degradation of dilead(II)lead(IV)oxide (Pb₃O₄) to tetragonal lead (II) oxide (PbO). Using a lower laser power resulted in a spectrum of red lead (Pb₃O₄) (Fig 5). This is consistent with historical records as being a pigment in common use at this time. Consequently lower power lasers are essential for application to painted textiles.

It was evident that focusing onto a rough painted fabric resulted in a reduction of collected Raman intensity producing in a highly degraded spectrum [33]. However raising the microscope stage around 5 mm from the point of best visible focus when using the 50x lens led to an improvement in the quality of the signal when the spectrometer was set in confocal mode. This is because the confocal volume from which the Raman scattered photons are being collected is then fully immersed in the pigment layer and thus the Raman scattered intensity is maximised [33].

Using a long wavelength (near infrared) laser reduces the fluorescence but increases the likelihood of pigments which absorb strongly in this region, e.g. the blue pigments in particular, overheating. Lower laser power is required to prevent this. The resulting reduction in spectrum quality can be offset by increasing the number of scans undertaken. However it was found that 10 ten-second accumulations generally provided acceptable spectrum quality.

The presence of Prussian blue in the blue flower (Fig 2) is of particular interest. It was the first modern synthetic pigment and is recorded as patented in 1704. The chair cover was painted in China so it is evident that this work will be extended to characterize binders, surface finishes and even natural soiling. This marriage of science with art should serve to preserve our heritage more effectively in museums and collections around the world.

It is evident that Raman microspectroscopic techniques can be successfully applied to the identification of pigments used on historic painted textiles. Low laser power and short exposure have been shown to allow unambiguous pigment identification, while assuring no damage to the artifact. Operating in confocal mode improves the spectral quality, principally by reducing the amount of background fluorescence picked up. These analyses, involving, typically, a combination of techniques, will allow deeper comprehension of paint used on textiles, benefiting not only conservators but also museum curators and historians. To facilitate this, a database is being developed that is specific both to the pigments found on painted textiles and to the Raman laser wavelength used, as relative peak heights vary with different laser wavelengths.

To support informed conservation further, we are now turning our attention to the identification of consolidants and adhesives used during previous treatments, since artifacts are now being presented for necessary re-treatment, often without clear records of the techniques and materials used before. Eventually this work will be extended to characterize binders, surface finishes and even natural soiling. This marriage of science with art should serve to preserve our heritage more effectively in museums and collections around the world.

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**REFERENCES**


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