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An analytical Raman spectroscopic study of an important english oil painting of the 18th Century

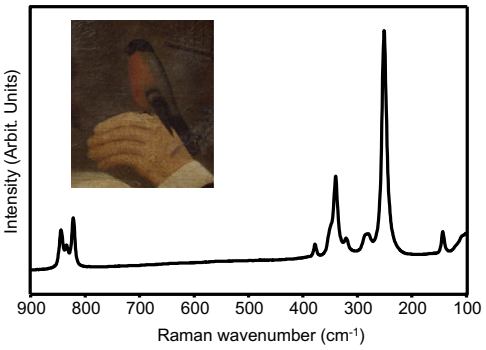
Howell G.M. Edwards [a,*], Peter Vandenabeele [b], Jan Jehlicka [c], Timothy J. Benoy [d]

[a] Chemical and Forensic Sciences, School of Life Sciences, University of Bradford, Bradford BD7 1DP, UK
[b] Laboratory for Archaeometry,Department of Archaeology, Faculty of Arts and Philosophy, University of Ghent, Sint-Pietersnieuwstraat 35, B-9000 Ghent, Belgium
[c] Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University, Albertov 6, 12843 Prague 2, Czech Republic
[d] The de Brecy Trust, de Brecy House, Lower Withington, Macclesfield, Cheshire SK11 9DF, UK

HIGHLIGHTS

- Raman spectroscopy for pigment identification in an 18th Century painting.
- First detection of a chromium mineral, hemihedrite, in an artwork.
- Combination of red pigments to achieve special tones.
- Attribution of powdered glass additive as a brightener.
- Possible characterisation of a Gainsborough palette.

GRAPHICAL ABSTRACT



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ABSTRACT

An opportunity was afforded to analyse pigment specimens from an unrestored oil painting in the style of the English School of the mid-18th Century prior to conservation being undertaken. Raman spectroscopy was adopted to characterise the pigments and indicated the presence of a novel red pigment which was assigned to the complex chromium mineral, hemihedrite, in addition to other interesting materials found in combination. This is the first recorded identification of hemihedrite spectral signals in an art context in a range of mineral pigments that are otherwise typical of this period and some hypotheses are presented to explain its presence based on its occurrence with associated mineral pigments. It is suggested that the presence of powdered glass identified in certain areas of the painting enhanced the reflectivity of the pigment matrix.

Introduction

The scientific analysis of artworks based upon the identification of pigments has been receiving much attention with the adoption of techniques that are either completely noninvasive or which otherwise require only minimal sampling and physical intervention [1–4] in this respect, Raman spectroscopy has provided a demonstrably important role for the characterisation of mineral and organic pigments and their binders from a molecular standpoint, reinforced by the chemical elemental information derived from other techniques such as X-ray fluorescence, X-ray diffraction, Laser Induced Breakdown Spectroscopy (LIBS) and Scanning Electron Microscopy SEM/EDAXS [5–8]. From such studies, although the correct historical provenancing of a painting is only achievable within a broad timescale because of the common

* Corresponding author.
E-mail address: h.g.m.edwards@bradford.ac.uk (H.G.M. Edwards).

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usage of pigments over hundreds of years [2], the exposure of fakes is often realised through the identification of rogue pigments that did not exist at the supposed time of creation of the art work. This idea may be succinctly stated [9] as follows:

> "Chemical analysis can never fully authenticate an art work but can expose a fake."

This is most certainly true and forms the basis of the forensic scientific analysis of art works; some very important landmark case-studies have appeared in the literature in recent years to verify this approach and to vindicate the use of spectroscopic analysis for the correct attribution of artworks to specific timelines, but always in association with historical provenancing wherever possible [10–12]. However, it is necessary to exercise some caution in the interpretation of scientific data relating to art works since unrecorded restoration of older artefacts and paintings could have been undertaken using only equivalent pigments to those originally employed or incorrect simulates. A classic case is the synthesis of Prussian blue, which was reported in the literature in 1704; hence, one may suspect that the evidence of finding Prussian blue in a supposedly early Renaissance painting of the 15th Century would automatically declare the painting to be a fake. However, the restoration of a blue pigment in a 15th Century painting that had suffered some damage at least some three hundred years later might be deemed to be normal procedure when the restorer naturally used what could be described as the best blue pigment then available, which may not have existed in the 15th Century [11].

What is not so clear is the recognition of synthetic mineral pigments with an established dateline for their preparation which are themselves often encountered as rare minerals; such cases are exemplified by crocoite, lead (II) chromate, and anatase, titanium (IV) oxide, which were synthesised in 1809 and 1923, respectively, yet both have been found in authentic art works and artefacts dating from many hundreds of years before these dates [13–16]. Despite this ambiguity, there is still expert opinion that dictates the discovery of these materials in an artwork immediately consigns it to the category of a fake [4,17,18], which has arisen mainly from a categoric statement by Gettens and Stout [19] to that effect.

A list of some synthetic pigment exemplars and their first recorded usage in art work is given in the literature [19]; their presence on an artefact or painting should not therefore imply this to be a fake *per se* but other factors should also be considered – and scientific analyses should always be accompanied by historical evidence and provenancing if possible.

In the current study, the discovery of a painting that on stylistic grounds appears to be an 18th Century portrait of the English School in an unrestored condition afforded a rare opportunity to carry out pigment analyses using Raman spectroscopy to determine their molecular composition; the information derived will then form the basis of a conservation strategy but will also possibly enable the artist to be identified from his palette.

Experimental

The "Bird in Hand" painting

This painting was acquired by the late George Lester Winward, a passionate collector of the genre, in 1977 at a sale of house contents in East Cheshire, UK, and now forms part of the de Brecy Trust art collection. It portrays a young man in 18th Century dress who has a bullfinch perched on his left wrist that he has seemingly released from its cage (Fig. 1). It has been favourably compared with the style of Thomas Gainsborough, 1727–1788, a renowned English portrait painter of the aristocracy and landscapes in the 18th Century. Gainsborough's palette is not reported in the open literature from previous conservation work carried out on his paintings and it is therefore of relevance to undertake a pigment study here.

Fig. 1. The 'Bird in hand' painting that was studied in this work. It portrays a young man in 18th Century dress who has a bullfinch perched on his left wrist that he has seemingly released from its cage.

The style of dress is appropriate [20] for that of an apprentice worker of the middle or working classes in the early to mid 18th Century rather than the aristocracy as deduced from the open-necked ruffled shirt, the cut of the jacket, the presence of natural hair rather than a wig and the buttoning of the breeches with absence of a fly; significant changes in dress were adopted in the period 1750–1800 and the overall style therefore fits in with an incised legend of "T G 1744" that can be seen in the lower part of the painting – this would concur with the idea that perhaps the painting is a self-portrait of Thomas Gainsborough as a young man of only modest means, in his candle-lit garret at the age of 17, when he was apprenticed to Hubert Gravelot, drawing master at the Royal Academy in London. The composition of the painting is very reminiscent of a later famous work by Sir Thomas Lawrence, *Master Lambton*: *The Red Boy*, the subject being Charles William Lambton, eldest son of the 1st Earl of Durham. There is circumstantial historical evidence that the "Bird in hand" painting was hanging in Wynnstay Hall, North Wales, ancestral home of the Watkin Williams-Wynn Family, at the time of Sir Thomas Lawrence's visits there relating to family portraits commissioned from him [21]; and that he could have possibly therefore based his pose for *"Master Lambton"* on the subject of our study. Little is known of the early life [22] of Gainsborough prior to his marriage in 1746 but it is thought that this naive painting style would have been typical of his earlier work [23].

It is reasonable to suppose from this provenancing that the painting under study could be placed in the mid-18th Century and might be an early self-portrait of Thomas Gainsborough; therefore, the identification of pigments from analytical Raman spectroscopy is a critical part of the scientific study that could support this chronology.