CONFOCAL RAMAN MICROSCOPY OF COLORANTS ON GLAZED OLD MASTER PORTRAITS

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Abstract: This contribution reports on the non-destructive, in situ identification of pigments used on old master drawings by means of confocal Raman microscopy.

The use of Raman microscopy for pigment identification is now well established and, indeed, the technique is at the forefront of those available when the pigment materials need to be analysed non-destructively and in situ [1]. Furthermore, the technique can even be applied to the analysis of pigments, which are on paintings or drawings that are covered by glass or other transparent materials.

Pigments that are embedded in glass can also be analysed by Raman microscopy. For example, we recently analysed some opacified red glass dating from the 9th–8th centuries BC that had been excavated from Nimrud in N. Iraq, identifying the red opacifier as cuprite, Cu$_2$O [2]. The same red opacifier was also identified in red studs dating from the 1st century BC in the native iron age in Britain. Yellow Anglo-Saxon beads dating from the 6th century AD have also been analysed by Raman microscopy, the yellow opacifier being identified as the lead tin yellow type II pigment, PbSn$_{1-x}$Si$_x$O$_3$ [2].

Confocal Raman microscopy is used for the kind of analysis mentioned above, because it is important to reject out-of-focus Raman scattered light that originates from outside the focal volume. The axial spatial resolution is a key parameter in this regard, which depends on the degree of confocality that can be achieved [3].

In more recent work we have analysed pigments on drawings by Hans Holbein that are mounted behind sheets of Plexiglas, poly(methyl methacrylate) which are used for protection. Holbein was the Royal portrait painter for King Henry VIII of England during two periods of the king’s reign viz. 1526-1528 and 1532-1543, painting both in miniature and in large.

Drawings by Holbein in the Royal collection at Windsor Castle have been analysed in order to identify the drawing materials that were used by Holbein during his time in the court of King Henry VIII. Among works that have been analysed from the collection are drawings of Thomas More, the Lord Chancellor at that time, and Jane Seymour, who was one of King Henry’s six wives. The purpose of the analysis was to compare the drawing materials on these portraits in the Royal collection at Windsor Castle with those identified on a drawing that belongs to the collection of the Victoria & Albert Museum. This drawing is thought to be the work of Holbein, but its provenance is not as well-documented as those of the Windsor Castle collection. Thus, the drawing was transported from the Victoria & Albert Museum in London to Windsor Castle so that it could be analysed along with the other drawings for comparison.

As expected for Holbein drawings, all the portraits have a chalk ground as was made evident by a Raman band seen at 1088 cm$^{-1}$, which is assigned to the symmetric stretching vibration of the CO$_3^{2-}$ anion of CaCO$_3$. Raman spectra of black pigments on the V&A drawing and one of the Windsor Castle drawings are compared in Fig. 1.
Fig. 1. Comparison of Raman spectra of the black pigment used on (a) the Victoria & Albert drawing and (b) the Windsor Castle drawing of Sir Thomas More. The laser excitation was equal to 632.8 nm.

As can be seen from Fig. 1, black pigments on both the Victoria & Albert drawing and the drawing of Sir Thomas More give rise to Raman bands around 1332 and 1580 cm\(^{-1}\). These can be assigned to the D and G bands of graphite, respectively. The sharpness of these bands suggest that the black pigment is polycrystalline graphite, rather than amorphous carbon, in both cases [4].

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References: