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Raman microscopy as a structural and analytical tool in the fields of art and archaeology ☆

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Abstract

The enormous strides that have been made at the Arts/Science interface by the meticulous application of Raman microscopy to the study of artwork and archaeological artefacts are outlined. Important recent case studies are presented to illustrate the power of the technique to answer key questions of great art historical, conservational, cultural, restorational, archaeological and scientific interest.

Keywords: Raman microscopy; Pigments; Manuscripts; Paintings; Archaeological artifacts; Dating; Attribution; Forgery

1. Introduction

The identification of pigments on manuscripts, paintings, enamels, ceramics, stuccoes, icons, polychromes, papyri, archaeological artefacts and glasses is critically important to the understanding of an object's history and in the resolution of problems related to restoration, conservation, dating and attribution of artwork. Many techniques, both molecular and elemental, have been used for these studies, though molecular ones are the more important. Raman microscopy (RM), significantly a molecular technique, has emerged in consequence of major recent advances in optics and detector technology as probably the most suitable of these techniques on account of its high spatial (~1 μm) and high spectral (~1 cm^{-1}) resolution, its molecular specificity, its excellent sensitivity by way of CCD (charge-coupled device) detectors, and the fact that most items may be analysed non-destructively and in situ [1]. Further, the introduction of small, portable spectrometer systems has enabled in some circumstances the instrument to be moved to the artwork rather than the artwork to the instrument; although this procedure does lead to significant loss of performance and convenience, it may be the best - indeed the only - option for the study of cave paintings and other immovable items of importance to our Cultural Heritage [2]. Recent important results obtained in the above areas will be discussed.

The identification of pigment degradation products on artwork is also a matter of great interest as studies addressing degradation pathways give insight into the nature of the environment in which the artwork or archaeological items have been held [3]. Some geological conversions, such as that of malachite to azurite, are very slow, but many chemical reactions taking place on artwork such as that of hydrogen sulfide with lead or copper pigments may be very fast. Whether the source of the hydrogen sulfide is atmospheric pollution or bacterial attack on sulfur-containing binders is not yet known. Other pigments and minerals may exist in more than one form, each of which has the component elements at sites of different symmetry. The combined application of infrared and Raman spectroscopy together with knowledge of the appropriate selection rules may then lead to ready identification of the particular form of the species which is present [4,5].

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2. Pigments

The immense literature on pigments is now well documented in standard reviews [1,6,7] and spectral libraries [8–10]. Most minerals are long established and have well defined structural and spectroscopic properties such as those relating to colour as a function of particle size, density, physical and chemical stability, etc. [11]. Synthetic pigments obviously have known first dates of manufacture, a feature that is key to the possible dating of illuminated manuscripts and paintings. That is, a synthetic pigment cannot appear on a work of art that supposedly predates the year of first manufacture of the pigment [9,10]. If it does, then either the work of art is a forgery (as in the case of certain papyri) [12] or it has been touched up at a later date (a matter which could be established with optical microscopy by identifying whether or not there is an underpaint).

It is important to emphasise that it is not possible to authenticate artwork ; thus in "The Logic of Scientific Discovery", originally published in 1934, Karl Popper postulates that scientific hypotheses can never be finally confirmed as true, and are acceptable only in so far as they manage to survive numerous attempts to falsify them [13]. The art world and especially auction houses often leave much to be desired in this context, frequently offering artwork and artefacts for sale without even testing for obvious signs of forgery [14].

3. Applications of Raman microscopy to manuscripts and artwork

Key features of recent Raman studies emanating from University College London on high profile manuscripts, artwork and artefacts will now be commented upon. All such studies involve the critically important establishment of palettes.

3.1. Lindisfarne Gospels (c. 715 AD) and related manuscripts

One of the world's foremost collections of Anglo-Saxon manuscripts, that at the British Library, had until recently been well studied from a palaeographical standpoint but barely at all with respect to the materials used in construction (pigments and binders). No Anglo-Saxon recipe books for artists' pigments are known to exist, and later ones – even price lists – were unreliable, being subject to mistranslation; moreover the terms used were and still are often ambiguous and/or used for more than one pigment. Notable is the Raman study [15] of the immensely valuable Lindisfarne Gospels, a work of art which to many represents the pinnacle of artistic achievement in manuscript illumination. Considered to have been created around 715 AD by the then Bishop of Lindisfarne in Northumbria, Eadfrith, in honour of St. Cuthbert who was himself Bishop of Lindisfarne from 685–687 AD, the major pages display fantastic complexity of zoomorphic interlace ornament as well as contrastingly simple evangelist portraits. The most significant of the identifications was that the blue pigment used is indigo ($C_{16}H_{10}N_2O_2$), which could have derived from the woad plant indigenous to England, not lazurite ($Na_8[Al_6Si_6O_{24}]S_n$) as had previously been believed. Lazurite in 715 AD was only known to have been found in the Badakshan mines in Afghanistan and it would seem highly unlikely that a trade route could have existed at that date between such mines and Northumbria. Hence the correct identification of the blue as indigo and not lazurite removed the need for such an unlikely proposition and resolved the matter. Several other extensive studies of Anglo-Saxon, early English and Carolingian manuscripts have also been carried out successfully by RM [15,16]. In addition, the semi-precious gemstones used to decorate the plates of silver attached to the oak cover of the Tours Gospel, "Evangelia Quatuor" (Fig. 1), were identified to be silica (SiO_2, white, cat's eye), emerald ($Be_3Al_2(Si_6O_{18})$, beryl, green, coloured with traces of Cr^{3+}), carbuncle ($Fe_3Al_2(SiO_4)_3$, iron garnet, red-brown), and sapphire (Al_2O_3, very pale blue, trace amounts of Cr^{3+}) [16].

Prior to Raman investigations, many unsubstantiated identifications made by purely visual means had become accepted as fact and reproduced uncritically. Thus the traditionally accepted triptych of the Insular palette, red lead

Fig. 1. Front cover of the Tours Gospel (c. 825 AD) showing the embossed plates of silver attached to the oak cover, the enamelled squares in each corner, and the 12 gemstones (labelled 1–12) attached to the silver plates [16].