RAMAN SPECTROSCOPIC ANALYSIS OF PIGMENTS FROM ROMAN VILLA EXCAVATIONS

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Abstract: Samples of Roman wall-paintings and pigment-vessels from Romano-British villas have been analysed by Raman spectroscopy and the minerals and mixtures used to obtain the different colours and tonalities have been identified.

Numerous wall-paintings and five fragmentary ceramic pots containing pigments, all of them belonging to four Romano-British villa sites near Northampton, situated in the Nene Valley and dating from ca 200 AD, have been analysed by Raman spectroscopy.

The predominant colours on the samples of wall-paintings are red and grey; both of these are used in a wide range of tonalities, followed by white and yellow and by the less common green and blue colours.

Of particular importance in these sites is the occurrence of ceramic vessels with remains of pigments (red, yellow, white and brown), specifically because of the comparison that can be made with the Raman analyses at other Romano-British villa sites [1,2].

Samples have been analysed by both conventional Raman and FT-Raman spectroscopy.

FT-Raman spectra were recorded with a Bruker IFS66 spectrometer with FRA 106 Raman module attachment and dedicated microscope. The laser excitation wavelength was at 1064 nm using a Nd⁺³/YAG laser. The spectral resolution was 4 cm⁻¹ and from 2000 to 4000 scans were accumulated to improve the signal-to-noise ratio.

For conventional Raman analyses a Renishaw inVia Raman Microscope coupled to a Leica DMLM microscope with 20X, 50X objective lenses operating at 785 and 488 nm laser wavelengths was utilized. 30-40 accumulations at 10 seconds exposure time with a laser power between 0.5 to 50 mW were typically used to collect spectra.

In spite of the rather small variety of pigments at these sites, the richness of the tonalities present in the paintings has been obtained by mixtures of the main pigment (for example, haematite for the red colour, carbon for grey and limonite for the yellow colour) with carbon to make the colour darker or calcite to lighten it. As a result, the colours in the wall paintings include red, orange, pink, yellow, brown, black, grey, white and different tonalities of blue and green.

Several remarkable differences have been found among the pigments used in the villas. Whereas caput mortuum [3] appears in both the Horestone Brook and Whitehall Farm villas it is absent in the Easton Maudit and Castor villas. Cinnabar, an expensive but desirable red pigment in Roman Italy [4], is absent from these sites.
Blue and green colours are uncommon pigments in this province of the Roman Empire. Cuprorivaite and green earth appear in Horestone Brook and Whitehall Farm villas for the blue and green colours, respectively, whereas in the Easton Maudit and Castor villas only malachite has been found.

Carbon for the black colour, calcite for white and a mixture of both pigments in a wide range of proportions was used to obtain different tonalities of grey.

The most remarkable occurrence found in the vessel pigments is the presence of anatase, a titanium dioxide polymorph with rutile, which is the more common mineral. It is the first time that anatase has been found among the pigment compositions used in the Roman Empire. Its appearance is controversial because there are no references that it was ever used as a pigment in ancient times [5,6].

The selection of pigments is probably due to a change on fashion, the availability of the pigments in the provincial region, the purchasing power or, perhaps, to different techniques used by the painters.

References: