Spectral transparency of historic artists' pigments

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Introduction

Following the invention of infrared reflectography (IRR) for the imaging of underdrawings, studies have been conducted to determine directly or indirectly the optimum spectral window for IRR (van Asperen de Boer 1969; Delaney *et al.* 1993, 2005). However, there has not been a comprehensive survey of the transparency of historic artists' pigments over the full near infrared (NIR) range. The recent developments of another non-invasive imaging technique, optical coherence tomography (OCT), which enables non-contact imaging of the stratigraphy of paint layers, has prompted a renewed interest in studying the transparency of pigments in the NIR range (Liang *et al.* 2004, 2005a; Targowski *et al.* 2004; Szkulmowska *et al.* 2007).

A set of paint-outs consisting of a wide variety of historic artist's pigments (~50) in both egg tempera and linseed oil has been prepared. The pigments were chosen to be representative of what is found on paintings, and the compositions of the pigments were verified with energy-dispersive X-ray analysis (EDX), Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD). The samples were prepared with known pigment volume concentration and thickness. In order to measure the transparency of the paint layers, one set of paint-outs was prepared over thin glass microscope slides.

Spectral measurements

In order to determine the best spectral windows for NIR imaging, either to reveal underdrawings in the case of IRR or to penetrate deeper into the paint layers in the case of non-contact cross-section imaging using OCT, the relative spectral transparency of the paint samples needs to be measured. The transparency of a paint layer depends on both the scattering and absorption properties, since light is both scattered and absorbed when it travels through the layer. For paint layers, the depth range of OCT is limited by multiple scattering rather than absorption, since OCT has high sensitivity and dynamic range. For a strongly scattering paint layer (painted on glass), we expect to find the backscattered light and hence the reflectance to be high, and independent of whether the sample was placed on a white or black background. A highly absorbing paint layer would have low reflectance on a white or black background. In contrast, a highly transparent layer will have high reflectance when it is placed on a white background but low reflectance when placed over a black background.

An Ocean Optics HR2000 fibre optic spectrometer (200–1100 nm), a Polychromix DTS 1700 (900–1700 nm) and DTS 2500 (1700–2500 nm) fibre optic spectrometer were used to measure the spectra between 400 and 2500 nm. The spectral resolutions of the three spectrometers are 0.9, 12 and 22 nm respectively.

Results and conclusions

By comparing the spectral reflectance over white and over black, we find that almost without exception all paint samples have best transparency (or least extinction) at ~2.2 μm. There are six pigments that have slightly better (but comparable) transparency in other regions of the spectra. The general trend is that the pigments in linseed oil or egg tempera are more transparent with increasing wavelength over the VIS-NIR spectral range.

This comprehensive survey of VIS-NIR reflectance spectra also provides a reference library for the identification of historic artists' pigments. By extending the wavelength range into the NIR, additional spectral features that are unique to each pigment are revealed, allowing more conclusive identification (Bayerer 1996; Bacci 2000; Liang *et al.* 2005b). The positions of the peaks in the spectra are found to shift whenever the concentration or the particle sizes changes, which needs to be considered when identifying pigments based on their spectra. The successes and limitations of non-invasive identification of pigments on actual paintings using this VIS-NIR reference spectral library along with newly developed algorithms for spectral identification will be reported in a future publication.

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