Pigment identification with optical coherence tomography and multispectral imaging

H. Liang, K. Keita, B. Peric, T. Vajzovic

Nottingham Trent University, School of Science & Technology
Clifton Lane, Nottingham NG11 8NS, UK
E-mail: haida.liang@ntu.ac.uk

ABSTRACT

We describe a new method for non-invasive pigment identification by combining the spectral reflectance in the visible spectrum with near infrared OCT cross-section images of the subsurface layer structure.

Keywords: optical coherence tomography, multispectral imaging, spectral imaging, pigment identification, scattering coefficient

1. INTRODUCTION

Routine identification of pigments on a painting or painted object is carried out in museums by taking a tiny sample to examine under a microscope. To identify pigments in various layers, the sample is prepared and polished to examine the cross-section. An experienced microscopist can visually identify the pigments according to their colour and shape. The disadvantage of the method is that it is invasive and conservation ethics restricts sampling to regions of damage or edges of the art work, hence it is difficult to obtain a global view of the material composition of the whole piece.

It has long been recognised that spectral reflectance can be used as a signature of a pigment to offer non-invasive identification of pigments. For the last 10 years, multispectral imaging which offers an efficient measurement of spectral reflectance over a large area has been used for spectral pigment identification[1,2]. However, this non-invasive technique has not been met with enthusiasm in the conservation community partly because the identification of mixtures of pigments is unreliable and it cannot identify a pigment if it has deteriorated. The difference between spectral pigment identification and the examination of a sample under a microscope is that the latter offers not only colour but shape information whereas spectral pigment identification gives spectral (hence colour) information but without any shape information on the pigment particles.

Recently, another non-invasive imaging technique, optical coherence tomography (OCT), has been successfully applied to the imaging of subsurface paint layers[3-9]. It has been shown that in certain cases where the paint is transparent and if the pigment particles are of a few microns in size, it is possible to see the individual particles[5,9]. Even when it is not possible to see the individual particles, the scattering properties of the paint will contribute additional information to the identification of the material. Since paint is more transparent in the near infrared and most efficient OCT sources are in the near infrared, it is preferable to use an infrared OCT rather than an OCT that operates in the visible range. Unlike cross-sections of paint samples viewed under a microscope, OCT cross-section images do not have colour information. However, a combination of OCT images of paint cross-section and multispectral imaging of

the same area can yield structural and spectral (hence colour) information non-invasively. In addition, even when the pigment particles can not be resolved by the OCT, the scattering and absorption properties can be still be measured from the OCT cross-section images. This additional information can also assist spectral pigment identification.

We will show in this paper to what extent the combination of OCT imaging with multispectral imaging can be used to identify pigments. We will use the novel portable multispectral camera, PRISMS[10] (Portable Remote Imaging System for Multispectral Scanning) for spectral pigment identification.

2. SPECTRAL PIGMENT IDENTIFICATION

A paint consists of pigments in a binding medium. A given type of pigment can be painted out in different binding medium, concentration, particle size, thickness and roughness. In order to identify a pigment through the spectral reflectance of its paint, it is important to distinguish the spectral features of the pigment from variations due to the above factors. In the following section, we examine the effects on the spectral reflectance as a result of each of these variations.

Figures 1 to 5 show that none of the above variations change the key spectral features significantly, i.e. the position of the peaks associated with a pigment type. Incomplete hiding of paint layer does not change the spectral reflectance significantly. Positions of the peaks can shift by ~20nm with concentration, particle size and binding media. Binding medium gives the greatest variation in spectra changing the relative height between peaks, but the basic characteristics of the spectra are still preserved. Finally, the application of paint by hand gives similar spectral reflectance when painted by the same person in the same manner. This shows that the key spectral features in a reflectance spectrum is mostly determined by the pigments in the paint, at least for the spectral range 400-1000nm. For this reason, the identification of pigments in single pigment paint mixtures in paintings has been successful as long as there is no deterioration[1,2,13].

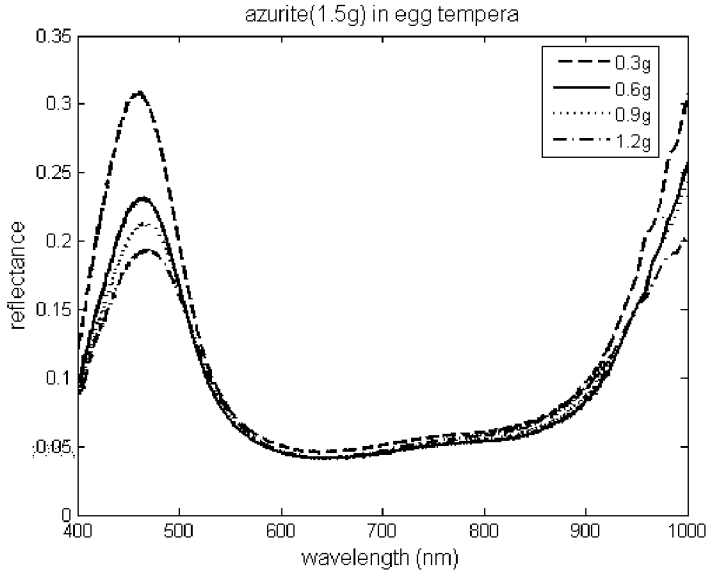
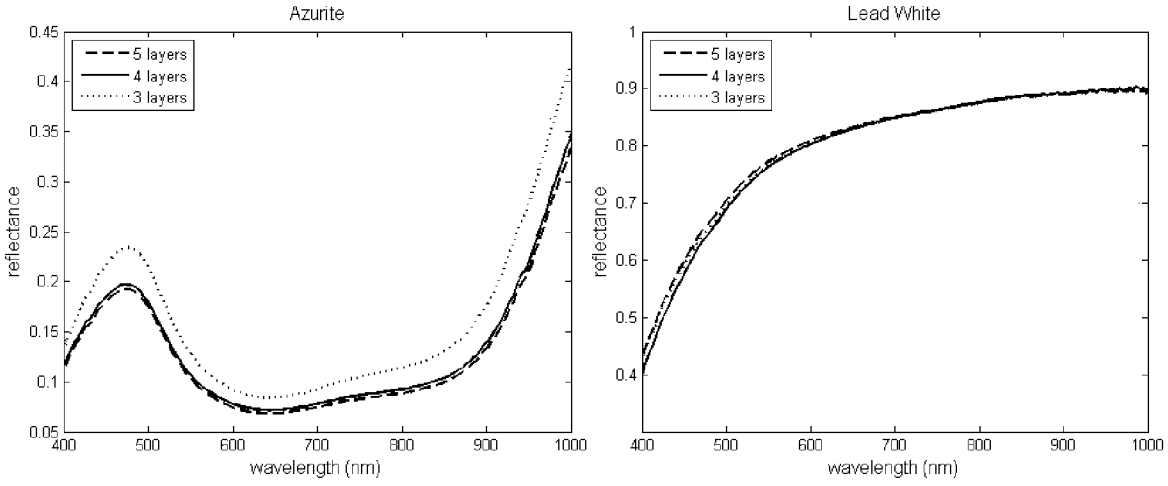
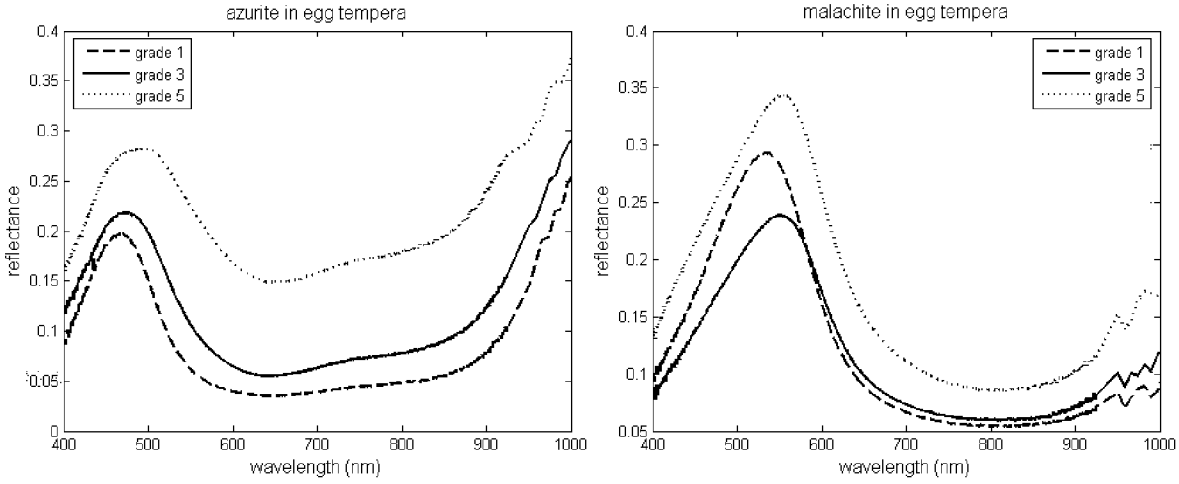


Figure 1. Spectral reflectance of paint consisting of various concentrations of azurite pigments in an egg tempera binding medium. The legends indicate the amount of egg tempera added to 1.5g of azurite.



(a) (b)

Figure 2. Effect of thickness of paint on the spectral reflectance of a) azurite in egg tempera and b) lead white in egg tempera (the higher the number of layers the thicker the final paint layer).



(a) (b)

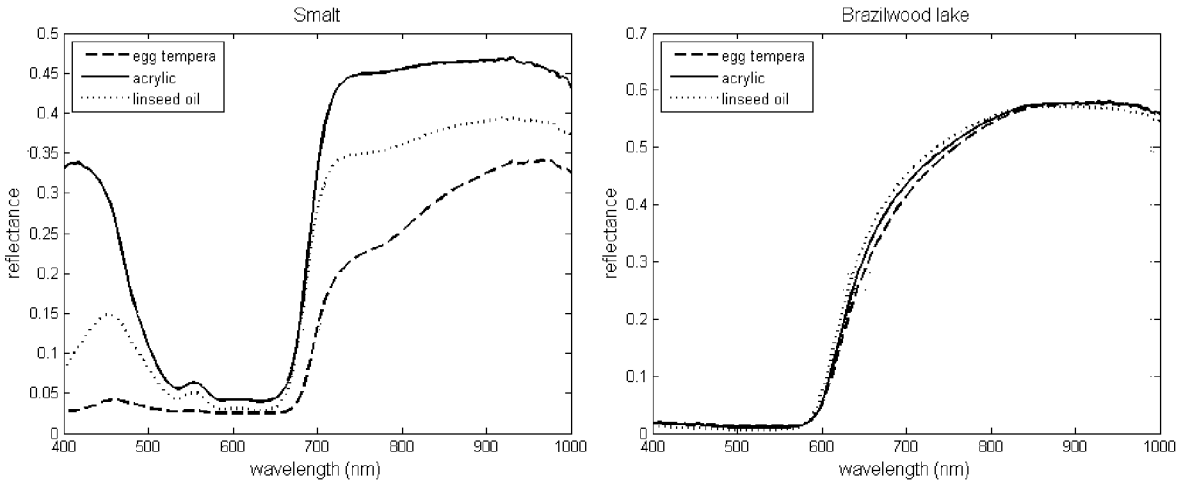
Figure 3. Effect of particle size on the spectral reflectance of paint: a) azurite in egg tempera and b) malachite in egg tempera with 3 different particle sizes. Particle size decreases with increasing grade.

For pigment identification involving paint mixtures, Kubelka-Munk (KM) theory[11] provides a convenient way of modelling the expected reflectance from a paint layer consisting a mixture of pigments[13]. The KM theory is a simple approximation to the full radiative transfer model, where the diffuse reflectance (R) of the layer without interfaces is related to the effective absorption (K) and scattering coefficients (S) through

$$R = \frac{1 - R_g[a - b\coth(bSh)]}{a + b\coth(bSh) - R_g},$$

where $a = \frac{K+S}{S}$, $b = \sqrt{a^2 - 1}$, h is the layer thickness and R_g is the reflectance of the substrate. KM theory assumes diffuse illumination and collection, however, in practice measurements are often made with collimated normal illumination. Saunderson's correction[12] is normally applied to correct for the reflection at the air/paint and paint/air interfaces. If it is possible to measure the reflectance of the same paint layer over a black and white substrate,

then K/S can be deduced. For a paint layer with infinite optical thickness, the diffuse reflectance is directly related to *K/S*.



(a) (b)

Figure 4. Effect of binding media on the spectral reflectance of paint: a) smalt pigment and b) Brazil wood lake pigment in an egg tempera, linseed oil and acrylic binding medium.

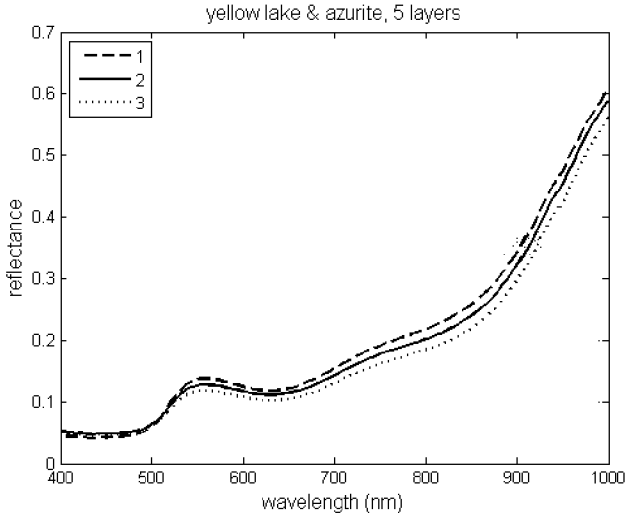
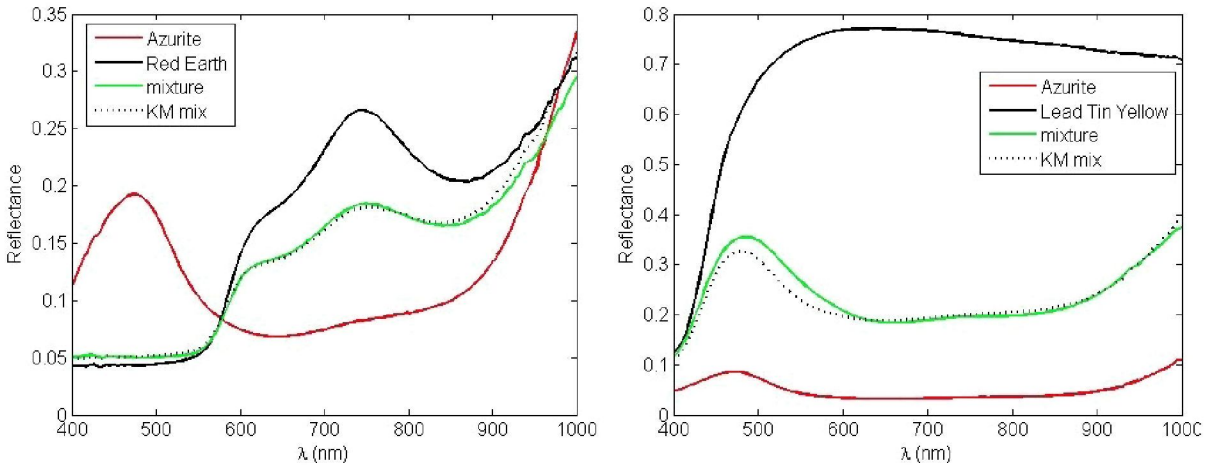


Figure 5. Spectral reflectance of 3 paint patches of Buckthorn lake mixed with azurite in egg tempera painted on 3 separate occasions by the same person. Each paint patch was painted in 5 layers.

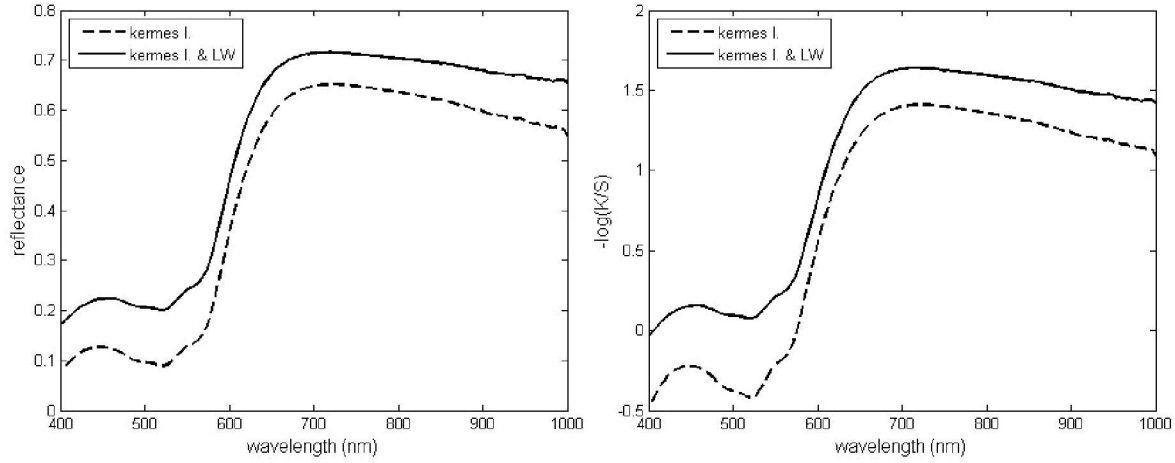
If a mixture of different paint components can be modelled as a linear combination of *K/S*, then we can predict the reflectance of the paint mixture. In this case, log(*K/S*) versus wavelength curves shift by a constant for different concentrations which means that the shape of log(K/S) is concentration invariant. To verify how well KM theory can predict the spectral shape of paint mixtures, a set of single pigment paints and their mixtures were painted out and measured with an Ocean Optics fibre optic spectrometer (HR2000) with normal illumination and 45° collection. The measured single pigment spectral reflectances were used to predict the spectra of the mixtures using KM theory. Since our aim here is to identify the pigments in a mixture, the concentrations of the single pigments were set as free parameters to find the best fit of the predicted spectrum to the actual measured spectrum of the mixture. Figure 6 shows a couple of examples of two pigment mixtures where the KM theory with the appropriate concentrations of each pigment is able to give a spectrum very similar to the actual measured spectrum of the mixture. It is found that in general the method works well except when highly

absorbing blue pigments like Prussian blue and indigo are involved. However, by increasing the relative strength of scattering to absorption by adding lead white to the highly absorbing pigment and treating the white added mixture as one component, the method works again. Based on the above study, an algorithm is devised to automatically identify pigments by fitting different combinations to the unknown spectrum. The best fit for each combination is then cross-correlated with the unknown spectrum. The best identification is the one with the highest normalised cross-correlation coefficient at zero offset. An extra 20 nm range around zero offset should be allowed to account for the slight shift in peaks due to different binding medium, concentration and particle size. When the algorithm was applied to 7 two pigment paint mixtures, at least one of the two pigments was identified correctly in each case and in two cases both pigments were identified correctly.



(a) (b)

Figure 6. Kubelka-Munk theory predicting mixture of pigments. The dotted curve gives the predicted spectrum and the green curve give the measured spectrum of the actual mix. a) Measured reflectance of azurite (red), red earth (solid black) and a mixture of the two (green) in egg tempera compared with the predicted spectrum (dotted black) b) measured reflectance of azurite (red), lead tin yellow (solid black) and a mixture of the two (green) compared with the predicted spectrum (dotted black).



(a) (b)

Figure 7. a) measured reflectance of kermes lake pigment in linseed oil (dashed) and kermes lake mixed with lead white in linseed oil (solid) b) same as a) but plotted in terms of -log(K/S).

The reason for the incorrect identification is that two different pigment combinations can sometimes give spectra with similar shape. A simple example is given in Figure 7 where the spectral shape of kermes lake painted over a white substrate and kermes lake mixed with lead

white are similar. However, we know that the scattering properties of the two are very different. If we have a paint layer painted over a transparent material such as glass, then it is possible to measure K and S using KM theory by measuring the reflectance over a white and a black background. However, this is not possible on a painting as the substrate is typically opaque. The following section shows a method of measuring the scattering properties non-invasively on a painting.

3. COMBINED OCT AND MUTISPECTRAL IMAGING FOR PIGMENT IDENTIFICATION

A Fourier domain OCT (Thorlabs SROCT) at 930nm was used for the non-invasive imaging of paint layers. It has a 9μm transverse resolution and a 6μm depth resolution (in air). Figure 8 shows the cross-section images obtained with the OCT of a highly absorbing pigment (charcoal), a weakly scattering and absorbing pigment (sappon wood lake), a medium scattering and absorbing pigment (artificial ultramarine dark) and a highly scattering pigment (Ti white). OCT readily shows the scattering and absorption properties of paint layers. Figure 9 shows that while kermes lake and kermes lake mixed with lead white have similar shape in spectral reflectance, their scattering properties are very different as shown in their OCT images.

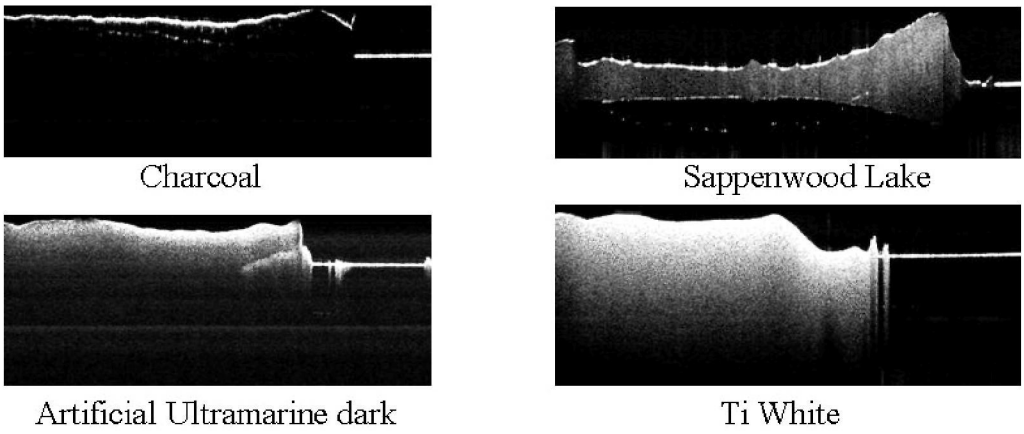


Figure 8. OCT cross-section images of various pigments (in a linseed oil binding medium) painted on glass microscope slides.

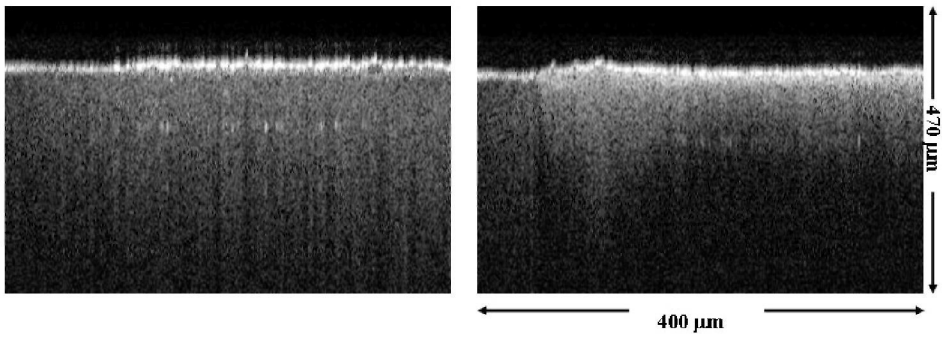


Figure 9. OCT cross-section images of a) Kermes lake in linseed oil (~8 μm thick layer); b) lake with lead white in linseed oil (~12 μm thick layer) painted on a white Teflon board (short section on the left of the images are regions of bare Teflon). The faint dotted lines in the middle of the images are ghost images.

PRISMS[6] (Portable Remote Imaging System for Multispectral Scanning) was originally designed for in situ remote high resolution multispectral imaging of wall paintings from the

ground level. It consists of a filter system operating between 400nm and 880nm (9 filters evenly spaced between 400 and 800nm with 40nm bandwidth and one filter at 880nm with 70nm bandwidth) and a CCD camera mounted on a small telescope. Since this is a multispectral camera designed in our lab and readily available, we used it in combination with the Thorlabs OCT at 930nm to image an easel painting to demonstrate the advantages of combining OCT with multispectral imaging for pigment identification. PRISMS was place 6m from the painting giving an image resolution of ~45μm per pixel on the painting. The OCT probe was placed 1cm from the painting surface on a motorised X-Y-Z micrometer stage to scan a 1cm by 2.5cm area. The individual cross-section images are stacked together and resliced in the plane parallel to the paint surface to give an en face image. Figure 10 shows a direct comparison of the multispectral image at 880nm and the OCT image at 930nm of a painting. The OCT with 5 times better resolution shows more clearly the brush strokes.

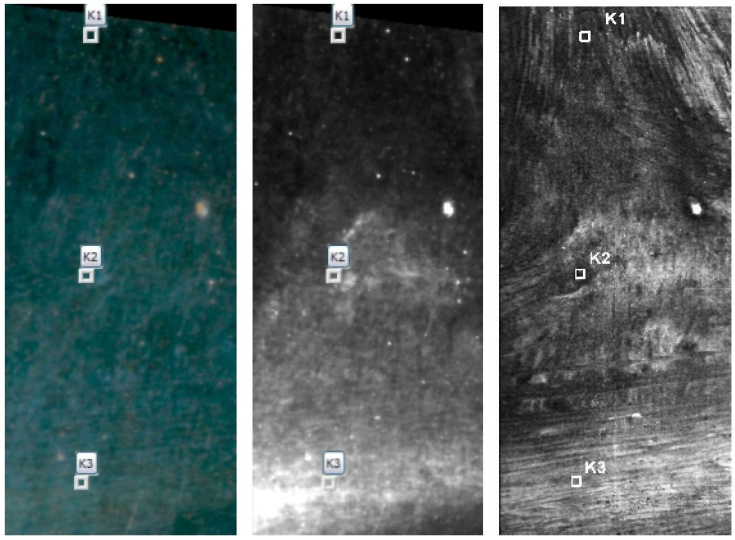


Figure 10. Multispectral image and *en-face* OCT image of the virgin's blue cloak in *Virgin and Child with an Angel* by an imitator of Francia (National gallery NG 3927). a) colour image deduced from the multispectral image cube assuming D65 illumination and 1931 2° standard observer; b) 880nm image from PRISMS; c) *en face* OCT image at 930nm. The images are 1cm by 2.5cm.

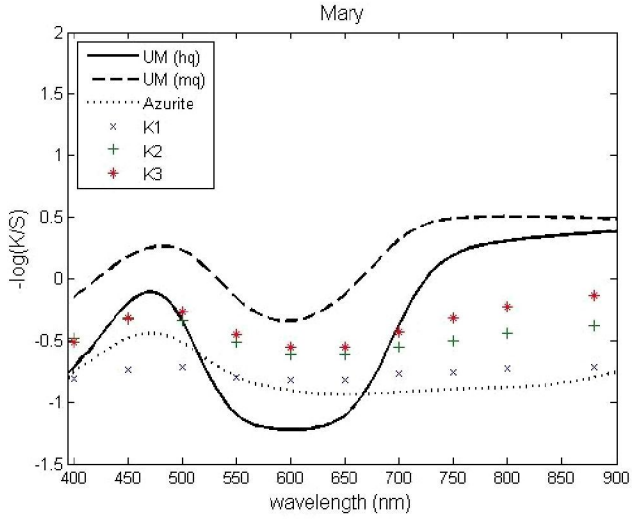


Figure 11. Spectral reflectance converted to –log(*K*/*S*) measured with PRISMS at positions marked in Fig. 10 compared with spectral reflectance of ultramarine and azurite from a reference library.

Figure 11 shows the spectra corresponding to 3 different locations indicated in Fig.10 obtained from a multispectral image cube captured by PRISMS along with spectral reflectance of known pigments in linseed oil. While the spectra do not agree with either azurite or ultramarine, they seem to have spectral features more in common with ultramarine. OCT images at the same locations show that the shadow areas to be more absorbing than pure ultramarine and the high light area to be more scattering than pure ultramarine (see Fig. 12). It is likely that the shadow areas are painted with ultramarine mixed with a highly absorbing black pigment and the highlight to be ultramarine mixed with a highly scattering white pigment. Figure 13 shows the spectrum in the shadow area K1 agrees better with ultramarine mixed with charcoal than pure ultramarine or azurite mixed with charcoal. The spectra of ultramarine and azurite mixed with charcoal were calculated from KM theory. Similarly, the spectrum at K3 agrees better with ultramarine mixed with white than azurite mixed with white. Microscopic images of sample cross-sections from a similar area on the painting showed that there are black and white pigments mixed with ultramarine (Helen Howard private communication).

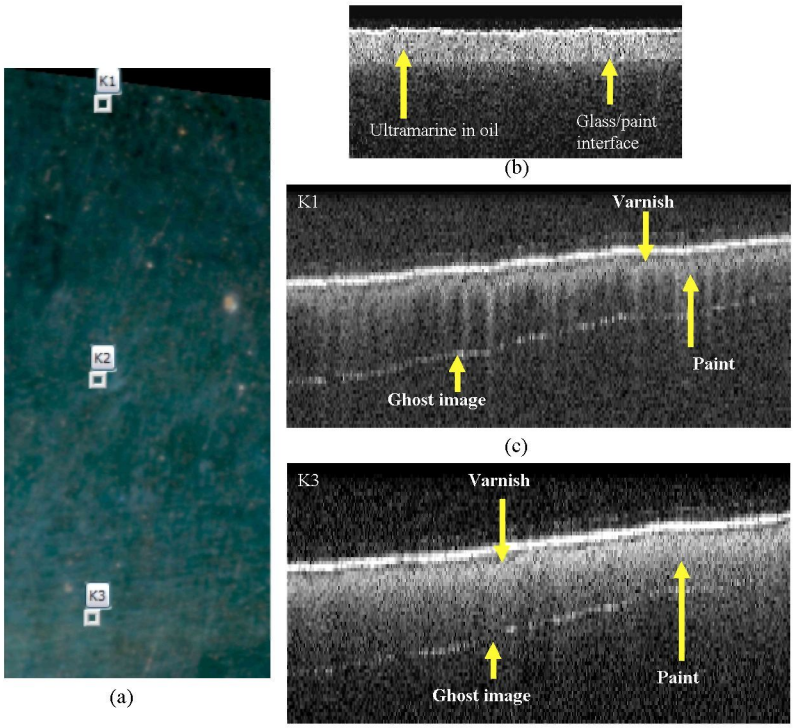
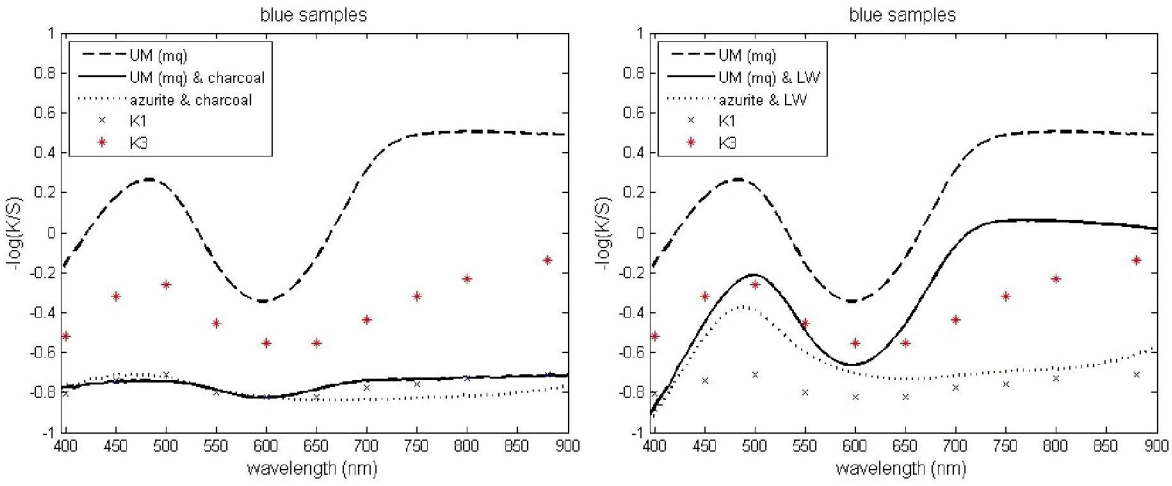


Figure 12. OCT cross-section image of the virgin's blue cloak in *Virgin and Child with an Angel* by an imitator of Francesco Francia (National gallery NG 3927). a) colour image of the blue area; b) an ultramarine in linseed oil paint layer over a glass microscope slide; c) an OCT cross-section image at K1 in the horizontal direction (1cm across and 600 μm in depth); d) same as c) but at K3.

4. CONCLUSIONS & FUTURE WORK

OCT combined with multispectral imaging gives both structural and spectral information for the paint layers. OCT assisted spectral pigment identification provides stronger constraints than spectral identification alone as it provides scattering and absorption information. Future development will involve quantitative measurements of effective scattering and absorption coefficients using OCT and multispectral imaging.

We would like to thank Marika Spring and Helen Howard from the National Gallery for providing information on the painting and sample analysis.



(a) (b)

Figure 13. Spectra of ultramarine, azurite mixed with a) charcoal and b) lead white compared with the measured spectra on the painting in the highlight area K3 and the shadow area K1. Note that the spectra for ultramarine mixed with lead white and azurite mixed with lead white was the best fit to the spectra at K3 using KM theory by setting the relative concentration as free parameters.. The same applies to the mixture with charcoal.

REFERENCES

1. S. Baronti, A., Casini, F., Lotti, S., Porcinai, 'Multispectral imaging system for the mapping of pigments in works of art by use of principal-component analysis', *Applied Optics*, vol. 37, pp.1299 (1998).
2. H. Liang, D. Saunders, J. Cupitt, 'A new multispectral imaging system for examining paintings', *Journal of Imaging Science & Technology*, vol. 49, pp.551 (2005a).
3. P.Targowski, B.,Rouba, M.,Wojtkowski, A.,Kowalczyk, 'The application of optical coherence tomography to non-destructive examination of museum objects', *Studies in Conservation*, vol. 49, pp.107 (2004).
4. H. Liang, M., Gomez Cid, R., Cucu, G., Dobre, D., Jackson, C., Pannell, J., Pedro, D., Saunders, A., Podoleanu, 'Application of OCT to examination of easel paintings', *Second European Workshop on Optical Fibre Sensors, Proc. SPIE*, vol. 5502, pp. 378 (2004).
5. H. Liang, M., Gomz Cid, R., Cucu, G., Dobre, A., Podoleanu, J., Pedro, D., Saunders, 'En-face Optical Coherence Tomography – a novel application of non-invasive imaging to art conservation', *Optics Express*, vol. 13, pp.6133-6144 (2005b) http://www.opticsexpress.org/abstract.cfm?id=85276
6. T. Arecchi, M. Bellini, C. Corsi, R. Fontana, M. Materazzi, L. Pezzati, and A. Tortora, "A new tool for painting diagnostics: Optical coherence tomography", *Opt. Spectrosc.*, vol. 101, pp. 23-26 (2006).
7. P. Targowski, G. Michalina, M. Wojtkowski, 'Optical coherence tomography for artwork diagnostics', *Laser Chemistry*, Article ID 35373 (2006).
8. H. Liang, B. Peric, M. Hughes, A. Podoleanu, M. Spring, and D. Saunders, "Optical coherence tomography for art conservation and archaeology", *Proc.SPIE*, vol. 6618, 661805 (2007).
9. G. Latour, J. Moreau, M. Elias, and J.-M. Frigerio, "Optical Coherence Tomography: non-destructive imaging and spectral information of pigments", *Proc. SPIE*, vol. 6618, 661806-9 (2007).

10. H. Liang, K. Keita, T., Vajzovic, 'PRISMS: A portable multispectral imaging system for remote in situ examination of wall paintings', in O3A: Optics for Arts, Architecture, and Archaeology, *Proc. SPIE*, vol. 6618, 661815 (2007).
11. P. Kubelka, "New contributions to the optics of intensely light scattering materials. Part I", *J. Opt. Soc. Am.*, vol. 38, pp.448-457 (1948).
12. J. L. Saunderson, *J. Opt. Soc. Am.*, vol. 32, pp.727-736 (1942).
13. R. Berns, J. Kreuger, M. Swicklik, 'Multiple pigment selection for inpainting using visible reflectance spectrophotometry', *Studies in Conservation*, vol. 47, pp. 46 (2002).