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There's more to reflectance spectroscopy than lux

Keywords

spectroscopy; reflectance; FORS; manuscripts; fibre-optic; probe

Introduction

Fibre-optic reflectance spectroscopy (FORS), is a well established technique employed to determine the reflectance spectra of artists' materials, such as pigments and paint binders, used in manuscripts or paintings.¹ The technique itself has been established for over 30 years and has been widely deployed for this purpose.² Reflectance spectra provide vital clues as to the identity of pigments employed in the works, the composition of mixtures of pigments and, in the case of near-infrared (NIR) data, hints as to what paint binders may have been used. The reflectance spectrum is typically obtained by illuminating a specific region of the object using a broadband light source, and the spectral profile of the diffusely scattered light is analysed to provide a measure of intensity vs. wavelength. The reflectance spectrum is generated by comparing the spectrum obtained from the sample with that from a white reference material and is normally expressed as a percentage of reflected light relative to the reference material, $R\%(\lambda)$, as the Kubelka–Munk function $F(R)$ or as $\log_{10}(1/R)$.³ The measurement is facilitated by the use of fibre-optic light-guides to direct the light onto the surface of the object under analysis, and back via a second fibre to the spectrometer, allowing the heavy and often large light source and detector to be located some distance away from the artwork. Spectra in the UV to NIR spectral region (300–1100nm) are readily recorded using relatively low-cost silicon CCD detectors coupled to a spectrograph. Longer wavelengths can be accessed using either a spectrograph and InGaAs CCD NIR camera, a scanning spectrometer and single point detector or a Fourier Transform spectrometer. These devices are capable of recording spectra with wavelengths up to 2600nm if using extended InGaAs detectors.⁴ Various commercial spectrometer systems are available which employ multiple spectrometer stages and in conjunction with suitable lamps and probes allow the study of reflectance spectra over the range 350–2500nm, such as, for example, the PANalytical FieldSpec® range of field spectrometers. Finally many research groups use bespoke spectrometer designs but provide varied degrees of detail regarding their instruments' specifications and performance.⁵

One of the most important considerations of any FORS instrument is the design and performance of the probes, which illuminate the area of interest and collect the back-scattered light. There are a wide range of designs used: a key feature is that the illuminating fibre(s) fully illuminate the area from which the scattered light is collected and that specular reflections from the surface are not collected. Any contribution from scattered ambient light should be eliminated, either by eliminating it from the measurement completely by recording spectra under subdued lighting or by fully taking its contribution when calculating the spectra. A common probe design comprises a bifurcated bundle of fibres that terminate in a single probe head.

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1 See, for example, Mauro Bacci, Vito Cappellini and Roberto Carla, 'Diffuse Reflectance Spectroscopy: An Application to the Analysis of Art Works', *Journal of Photochemistry and Photobiology B: Biology* 1 (1987): 132–3; Paola Ricciardi, 'UV–visible–NIR Reflectance Spectrophotometry in Cultural Heritage: Background Paper', *Analytical Methods* 8 (2016): 5894–6, http://www.rsc.org/images/TB_75_tcm18-249070.pdf (accessed 29 March 2018); Antonio Cosentino, 'FORS Spectral Database of Historical Pigments in Different Binders', *e-conservation Journal* 2 (2014): 53–65, <http://e-conservation.org/issue-2/36-FORS-spectral-database> (accessed 13 March 2018); Mauro Bacci, 'Fibre Optics Applications to Works of Art', *Sensors and Actuators B* 29 (1995): 190–6; Maurizio Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV–visible–NIR Reflectance Spectrophotometry', *Analytical Methods* 6 (2014): 1488–500; Mauro Aceto et al., 'Non-invasive Investigation on a VI Century Purple Codex from Brescia, Italy', *Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy* 117 (2014): 34–41; Mauro Aceto et al., 'Non-invasive Differentiation between Natural and Synthetic Ultramarine Blue Pigments by Means of 250–900nm FORS Analysis', *Analytical Methods* 5 (2013): 4184–89; Marco Leona and John Winter, 'Fiber Optics Reflectance Spectroscopy: A Unique Tool for the Investigation of Japanese Paintings', *Studies in Conservation* 46 (2001): 153–62; Marcello Picollo et al., 'Fiber Optics Reflectance Spectroscopy: A Non-destructive Technique for the Analysis of Works of Art', in *Optical Sensors and Microsystems, New Concepts, Materials, Technologies*, ed. Sergio Martellucci, Arthur N. Chester and Anna Grazia Mignani (New York: Kluwer, 2000), 259–65; Sotiria Kogou et al., 'A Holistic Multimodal Approach to the Non-invasive Analysis of Watercolour Paintings', *Applied Physics A, Special Issue on Paint-*

Some of the fibres are used to illuminate the area, whereas the others collect the reflected light and are coupled to the spectrometer. The output from the optical fibres typically has a numerical aperture of 0.22 which represents the range of angles over which the system can receive or emit light, meaning that the probe needs to be in close proximity (<10mm) to the surface in order to interrogate a small area and to collect a reasonable solid angle of the scattered light. When studying extremely fragile objects such as manuscripts it would also seem prudent to ensure that the probe does not come into contact with the surface of the page. However, in some published accounts probes are shown to be manually held in close proximity to the page,⁶ and where the optical design of probes requires short working distances, such as the 6mm specified in the IPERION CH mobile laboratory (MOLAB),⁷ careful mounting and manipulation of the probe must be ensured to protect the manuscript from accidental contact. Other probes illuminate the surface by the output of a single fibre, with the reflected light collected by a separate single fibre, with the two fibres held in a fixed configuration at a pre-defined angle by a rigid holder so as to prevent specular reflections. Such a probe may also employ collimating lenses but in order to provide spatial overlap of the two optical paths, and for optimum collection efficiency, the probe has to be almost in contact with the sample surface. For example, in the system demonstrated by the Cultural Heritage Science Open Source group, probes are held in intimate contact with the manuscript surface,⁸ and Mauro Bacci et al. reported on a system in which two fibres were used to illuminate the surface with incidence angles of 45°, and the collection optic held perpendicular to the surface. In order to arrange for correct alignment of the illumination spots and collection area they designed a hemispherical probe that made contact with the page via an o-ring used to exclude extraneous light. Such 'soft but stable contact' must be considered undesirable in accordance with contemporary conservation standards.⁹

Finally, a major consideration in instrumental design seldom discussed in detail by researchers or instrument manufacturers is the light dose to which the sampled area is subjected. For this, two factors need to be taken into account: firstly, the absolute power density to which the sample area is exposed, and secondly, the total overall exposure which can be considered as a product of the time taken for the alignment/acquisition of the spectrum and the spectral power density of the illuminating light source.

The negative effects of sample illumination are two-fold. Firstly, many organic dyes and some inorganic pigments, such as realgar, are photosensitive, undergoing chemical degradation as they are irradiated.¹⁰ This process is due to the unavoidable absorption of the illuminating light by the sample, and can only be mitigated by reducing the total light dose experienced by the sample to a minimum. A second factor is the heating of the sample during the measurement, caused by the absorption of light by the pigment, the binder or the substrate. Sample heating is often neglected and is not easily measured nor predicted. The amount of energy absorbed by the sample depends upon the absorption spectrum of the layers of pigment, binder, and of the substrate, the spectral profile of the excitation source and the rate of heat dissipation by the sample. The rate at which the illuminated region loses heat to its surroundings and cools is highly dependent upon the sample matrix and substrate. Localised sample heating can result from irradiation across the full spectral window to which the sample is subjected, including any UV and NIR/IR radiation from the illuminating lamp that falls beyond the range of the measurement itself.

In the conservation community a common measure of light intensity is the *illuminance*, measured using a light-meter and reported in units of lux (lumen m⁻²). It is important to consider the integrated light dose that any sample is subject to. In the British Standards Institution's *PAS198:2012*

ings: Analysis, Conservation and Interpretation 121 (2015): 999–1014.

2 Bacci, Cappellini and Carla, 'Diffuse Reflectance Spectroscopy'.

3 Ricciardi, 'UV-visible-NIR Reflectance Spectrophotometry'.

4 Ricciardi, 'UV-visible-NIR Reflectance Spectrophotometry'; John K. Delaney et al., 'Use of Imaging Spectroscopy, Fiber Optic Reflectance Spectroscopy, and X-ray Fluorescence to Map and Identify Pigments in Illuminated Manuscripts', *Studies in Conservation* 59, no. 2 (2014): 91–101.

5 Cf. Cosentino, 'FORS Spectral Database of Historical Pigments'; Bacci, 'Fibre Optics Applications to Works of Art'; Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts'; Aceto et al., 'Non-invasive Investigation on a VI Century Purple Codex'; Aceto et al., 'Non-invasive Differentiation between Natural and Synthetic Ultramarine Blue'; Leona and Winter, 'Fiber Optics Reflectance Spectroscopy'; Picollo et al., 'Fiber Optics Reflectance Spectroscopy'.

6 Cf. Ricciardi, 'UV-visible-NIR Reflectance Spectrophotometry'; Antonio Cosentino, 'FORS, Fiber Optics Reflectance Spectroscopy con gli spettrometri miniaturizzati per l'identificazione dei pigmenti', *Archeomatica* 1 (2014): 16–22; Constanza Cucci and Marcello Picollo, 'Reflectance Spectroscopy Safeguards Cultural Assets', online news item by the International Society for Optics and Photonics, 21 March 2013, <http://spie.org/newsroom/4721-reflectance-spectroscopy-safeguards-cultural-assets?SSO=1> (accessed 13 March 2018).

7 Cf. <http://www.iperionch.eu/project/fiber-optic-near-ftir/> (accessed 24 March 2018). MOLAB is part of the IPERION CH consortium formed to fulfil the Horizon 2020—Work Programme 2014–2015 for European research infrastructures, which calls for the establishment of a unique European research infrastructure for restoration and conservation of Cultural Heritage with an emphasis on Heritage Science.

8 Cosentino, 'FORS Spectral Database of Historical Pigments'.

9 Mauro Bacci et al., 'Non-Invasive Spectroscopic Measurements on the Il ritratto della figliastra by Giovanni Fattori: Identification of Pigments and Colorimetric Analysis', *Journal of Cultural Heritage* 4 (2003): 329–36; Bacci, 'Fibre Optics Applications to Works of Art'.

10 Andrea Macchia et al., 'Which Light for Cultural Heritage: Comparison of Light Sources with Respect to Realgar Photodegradation', *Journal of Applied Spectroscopy* 80 (2013): 637–43.

11 British Standards Institution, *PAS 198-2012 Specifications for Managing Environmental Conditions for Cultural Collections*, (2012), <https://shop.bsigroup.com/ProductDetail?pid=000000000030219669> (accessed 13 March 2018).

12 Personal communication by email between Stefan Michalski and David Howell, February 2018.

13 Paola Ricciardi et al., 'Near Infrared Reflectance Imaging Spectroscopy to Map Paint Binders In Situ on Illuminated Manuscripts', *Angewandte Chemie International Edition* 51 (2012): 5607–10.

Specification for Managing Environmental Conditions for Cultural Collections, it is recommended that under exhibition conditions a book is subject to as low a light level as practicable for viewing, typically at a level of 50lux.¹¹ In contrast, the lighting levels in a conservation studio may approach 1000lux over a few hours.¹² Thus, we can estimate that during a one month exhibition period or a day in a conservation studio a book may be subject to an integrated dose of 8000lux hr—and while in reporting FORS measurements few workers record the illuminance used, in one example the use of a 4000lux dose for a 5-second period, equivalent to a 5.5lux hr exposure, was recorded.¹³

The illuminance reported in units of lux measures the illumination intensity *as perceived by the human eye*, based upon the spectral (photopic) response of the cones in the eye, and only considering radiation in the range 400–700nm. It specifically does not take into account UV or NIR/IR radiation. For monochromatic light at the peak of the human eye's sensitivity, 555nm, an illuminance of 1lux, corresponds to an optical power density of 1.46mW m⁻². At longer and shorter wavelengths, where the eye is less sensitive, a correspondingly higher power density is required to give the same perceived brightness or illuminance. Taking the product of the photopic response for the eye and the spectral profile of a tungsten lamp operating at 3000K and integrating it over the range 400–700nm allows for the determination of the mean illuminance of the source as a function of the total power. This shows that, for the light source employed in this work, 1lux is equivalent to 4mW m in the range 400–700nm. This power density, which is higher than that for monochromatic green light, arises from the fact that the white light from the lamp contains significant levels of blue and red light to which the eye is much less sensitive (Fig. 1).

In this work we present a simple new design for a reflectance probe held on an adjustable arm and frame that operates at approximately 50mm from the surface of the object under analysis to permit the acquisition of spectra from a well defined target area of 2mm in diameter. The 'Team Pigment' FORS probe has been designed specifically for the safe study of manuscripts and other fragile works of art. The performance of this probe in the UV–vis and NIR range is reported. The true optical power density of this system—using a halogen lamp illuminator equipped with optical filters to limit the

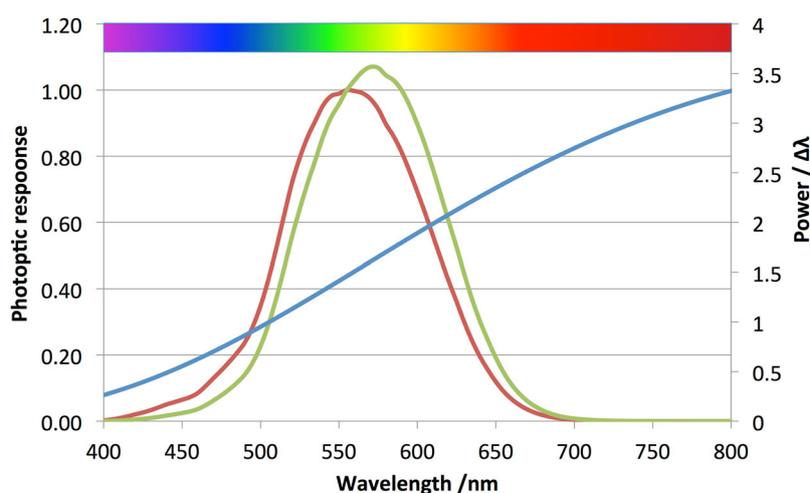


Fig. 1 The photopic response of the human eye (red) shown alongside the spectral output of a 3000K black-body radiator (blue) and the effective response of the eye to this light source (green). This demonstrates that across the visible spectrum the sensitivity of the eye varies significantly.

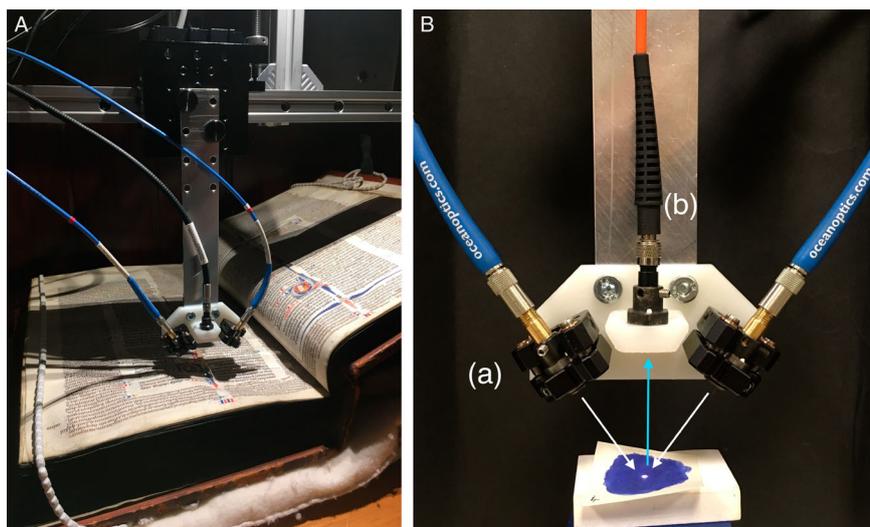


Fig. 2 'Team Pigment' FORS probe, *left*, showing head suspended from the gantry and the vertical adjustment system, *right*, the alignment of the two spots on a test sheet of blue paint. The single bright spot in the centre demonstrates the correct vertical alignment of the head for optimum collection efficiency.

illumination wavelength range—is measured and the thermal effects on model manuscripts established. These data are considered with regard to the potential for FORS measurements to cause localised sample heating and help establish power density thresholds for detectable temperature rises in the sample.

Experimental

We have designed a novel FORS probe in which the fibres and collimating optics are held some distance from the sample ensuring that accidental contact cannot occur. This provides precise control over the area being analysed and reproducible positioning of the probe above the sample, with a sampled area of approximately 2mm in diameter (Fig. 2).

The sample is illuminated by the output of a 20W tungsten light source (Ocean Optics HL-2000-HP) operating at 3000K equipped with a shutter, optional filter and attenuator. The light is delivered to the sample via a bifurcated fibre comprising of two high-OH 400 μ m silica cores. The outputs of the two fibres are focussed and arranged to overlap 5cm away from the probe assembly as shown in Fig. 1. The collimating lenses are adjusted so as to give an overlap region with a diameter of 2.6mm. The collection optics are held approximately normal to the sample surface and are comprised of a 100 μ m high-OH silica core optical fibre and collecting lens arranged so as to collect light scattered from the centre of the illuminated area with a diameter of 2mm. Employing three overlapping beams in this way allows the exact region under analysis to be identified visually and the vertical distance between the collection optic and the sample surface to be reproduced: when the sample is out of the focal plane of the collection fibre the two illuminating beams do not overlap. Importantly the overlap of the three beams occurs when the probe is held approximately 5cm above the plane of the page providing a safe stand-off distance from the manuscript.

The two illumination fibres and lens assemblies are mounted on kinematic mounts held on a 3D printed frame allowing for the simple alignment of the three beams. The frame itself is mounted on a vertical translation stage to permit the vertical positioning and fine-focussing of the probe assembly

on the sample. The translation stage is mounted on a linear slide that allows the smooth movement of the head from left to right. During a measurement the two spots of light generated by the two illuminating fibres are visible on the page. By adjusting the height of the probe above the surface the two beams can be brought together until they overlap and can be readily seen by eye. At this point the optical paths of the two illuminating beams and collection fibre are all overlapped and in focus giving the optimum reflectance signal. Such a precise vertical alignment enables the acquisition of reproducible and consistent data. A camera can also be added to the system to image the area under interrogation. The collected light is analysed in this system using a commercial CCD-spectrograph that provides excellent sensitivity in the 350–1100nm range with a spectral resolution of 3.5nm (Ocean Optics Maya-Pro, H1 grating). The system has many components in common with many FORS systems already in use, and is of comparable cost to those published elsewhere.¹⁴

14 Cf. Aceto et al., 'Non-invasive Differentiation between Natural and Synthetic Ultramarine Blue'; Cosentino, 'FORS, Fiber Optics Reflectance Spectroscopy con gli spettrometri miniaturizzati per l'identificazione dei pigmenti'.

15 Aceto et al., 'Non-invasive Differentiation between Natural and Synthetic Ultramarine Blue'.

For comparison a second system, based upon the design reported by Mauro Aceto et al. was assembled.¹⁵ It employs the same tungsten lamp (Ocean Optics HL-2000-HP) and CCD-spectrograph (Ocean Optics Maya-Pro, H1 grating) as described above. Like Aceto et al. we employed a bifurcated fibre probe comprising a hexagonal array of 600µm fibres acting as the illumination source, (Ocean Optics QP-600 UV-vis) and an additional central fibre as the collecting fibre. This probe can either be held in a block where the fibre bundle is held at a fixed distance and angle to the surface or as a free-standing item as illustrated in Fig. 3.

The power of the light source in the illuminated region was determined using a calibrated power meter equipped with a silicon photodiode head recording in the range 200–1100nm (Thorlabs S120-VC) and a high sensitivity thermal sensor capable of measuring the optical power in the range 200nm–10.6µm (Thorlabs S401C). The temperatures of model manuscript samples were measured using a FLIR-ONE thermal imaging camera (FLIR) capable of resolving the temperature of the illuminated area to within $\pm 0.1^\circ\text{C}$.



Fig. 3 Reflectance spectrometer based upon that published by Aceto et al. using a fibre probe to investigate a model manuscript surface, *left*, using sample block to ensure constant distance from the surface, in 45° geometry, and *right*, clamped 8mm above page in perpendicular geometry.

Model samples were created by grinding powdered pigments with water and gum Arabic or egg-white tempera to make a paint which was thinly applied onto substrates of 100gsm white cartridge paper or vellum and allowed to air-dry.

Results and discussion

1 Illumination conditions

The Team Pigment FORS probe illuminates an area of 2.6mm in diameter of a total area of 5mm². With an illuminance of 1250lux, a level considered to be acceptable for work in a conservation studio, the power density averaged over the visible spectrum (400–700nm) will be equivalent to 0.5mWcm⁻² of white light as generated by the tungsten lamp at 3000K, and corresponding to 25μW over the illuminated spot. Under these conditions the UV component of the lamp output, 350 λ <math><400\text{nm}</math>, is vanishingly small at <math><5\mu\text{Wcm}^{-2}</math>. This is less than the upper limit specified by the PAS 198 specifications for managing environmental conditions in cultural collections, which is 75μW/lumen and corresponds to 9.5μWcm⁻² at 1250lux.¹⁶

Using a 700nm short-pass filter to ensure that the illumination is in the range 350–700nm and placing the power meter at the intersection of the two illumination beams, the output from the lamp was adjusted using the attenuator to give 1250lux at the sample. Removing the optical filter, thereby allowing the full spectral lamp output range of 350–2600nm onto the power meter, increased the power density to 7mWcm⁻².

It is important to note that under both of these conditions the illuminance on the sample is 1250lux: the light level perceived by the human eye is the same. The difference is that in the unfiltered case there is a significant amount of invisible NIR radiation falling on the sample. We argue that this must not be neglected, as part of this radiation is absorbed by the sample and can cause heating and potentially damage the sample. This is discussed later in the article.

Placing a 1cm pathlength water filter in the light path has the effect of attenuating wavelengths of >1400nm and, whilst maintaining an illuminance of 1250lux, the power was measured as 120μW over the illuminated area, equivalent to 2.4mWcm⁻². The calculated spectral profile of a 3000K black body and the apparent spectrum after passage through a 1cm pathlength water filter are shown in Fig. 4.¹⁷ With the water filter in place the reflectance spectrum of a white Spectralon® reference sample was recorded. Under these light conditions a satisfactory signal level for recording reflectance spectra in the range 380–1100nm could be obtained employing a 100ms integration period on the spectrometer. As such, the spectrometer, with a 16-bit digitiser, yields a peak signal level of 40,000 counts, corresponding to approximately 60% saturation of the detector. Increasing the light intensity or integration time would have the effect of overloading the detector and preventing the measurement of spectra. Improved signal-to-noise ratios are obtained by averaging multiple acquisitions, and the data shown in Fig. 5 are the result of 4 × 100ms acquisitions.

To demonstrate the sample-to-sample reproducibility of the system, reflectance spectra were recorded from a standard photographic target—a QP Card 203—which comprises numerous squares of homogenous coloured pigment. The reflectance spectra from different areas of a single panel were recorded, and for each measurement a fresh white reference spectrum was also recorded and the probe head re-focussed upon the next sample. Using 16 × 100ms acquisitions the four spectra show a deviation of ±1% reflectance in the range 400–1050nm, demonstrating the outstanding stability and reproducibility of the Team Pigment system (see Fig. 6).

We conclude that using our instrument it is possible to record reflectance spectra with an illuminance of 1250lux, and a total light exposure for the

¹⁶ British Standards Institution, *PAS 198-2012 Specification for Managing Environmental Conditions for Cultural Collections*.

¹⁷ Cf. George M. Hale and Marvin R. Querry, 'Optical Constants of Water in the 200nm–200μm Wavelength Region', *Applied Optics* 12 (1973): 555–63.

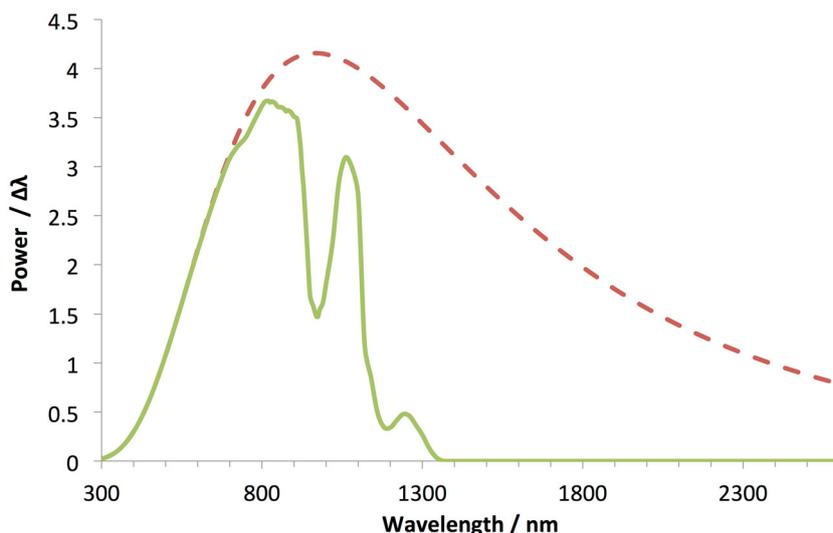


Fig. 4 Calculated spectrum from a 3000K black-body radiator (dotted red) and after passage through a 1cm pathlength water filter (green).

small area of the manuscript under investigation of less than 0.5lux hr for the measurement. This can be considered negligible compared to the light dose experienced under routine conservation or display conditions.

The second system, which was built to copy that described by Aceto et al., illuminates an area of the page using the output of a hexagonal array of fibres. With a working distance of 8mm from the surface of the page, the area illuminated is approximately 6mm in diameter and the central collection fibre collects light from an area of 4mm in diameter. Holding the probe either perpendicular or at 45° to the surface at a distance of 8mm and using a total power of 40μW for 350 < λ < 700nm gave a satisfactory signal intensity with a 100ms integration time, corresponding to approximately 40,000 counts, on the spectrometer. Under these conditions we calculate the illuminance to be 375lux, and this corresponds to 120μW in the range 350 < λ < 1100nm, and 160μW for 350 < λ < 1400nm (i.e. when using a 1cm pathlength water filter). The main difference between this second FORS spectrometer and that reported by Aceto et al. is the different model of spectrograph-CCD used. Aceto et al. used an Ocean Optics HR4000 which employs a CCD camera which has less than a quarter of the sensitivity of the one employed in the Ocean Optics Maya used in this work.¹⁸ As a result Aceto's system may have necessitated higher illumination power densities to obtain satisfactory spectra.

Although this second system allows the acquisition of spectra under low-level illumination, its configuration is not ideal as the divergent output of the bundled-fibre probe requires that it be maintained at exactly the same distance from the surface of the page to give a stable signal intensity. In this study, this was attempted by clamping the probe at a fixed distance perpendicular to the surface of the sample—however, we found that even small deviations in the vertical distance of the probe above the page, of the order of ±1mm, gave rise to a change of ±10% in the intensity of the reflected light and an instability in the reflectance spectrum. This shows that holding the probe above the surface by hand makes it impossible to accurately position the probe at the same distance for each measurement and hence gives rise to variation in the observed reflectance values. Finally, using the metal block supplied with the probe to facilitate holding the probe at the same distance for each measurement should be considered unacceptable for work on

¹⁸ Personal communication: conversation and email with Tony Boutle of Ocean Optics UK Ltd, February 2018.

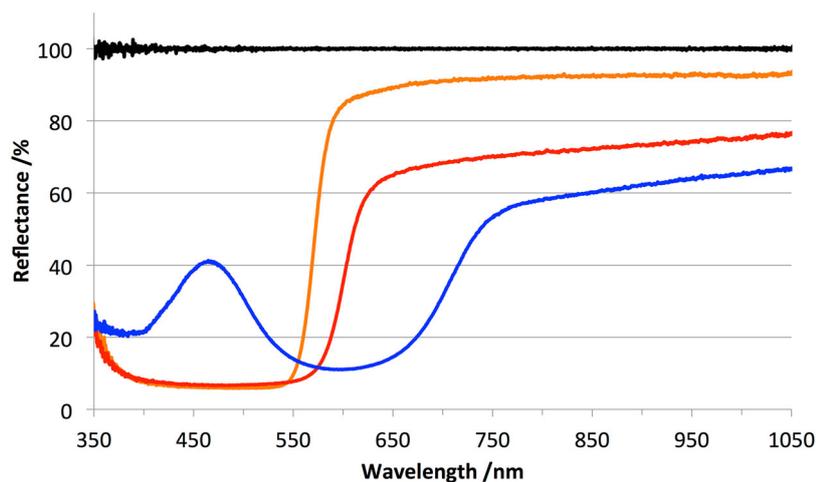


Fig. 5 Representative reflectance spectra obtained using new probe showing the spectra of red lead (orange), vermilion (red) and lapis lazuli (blue) paints on paper substrate. The black trace shows the reflectance spectrum of the Spectralon® tile, indicating a noise level of $\leq \pm 1\%$ in the range 380–1050nm. The conditions for these were $4 \times 100\text{ms}$ acquisitions.

manuscripts since it requires the block to be in contact with the surface of the page. Even if a protecting sheet is placed between the block and a manuscript page, the pressure of the contact may cause damage and so should be avoided. The alternative approach of holding the probe in close proximity to the page is potentially hazardous and liable to variations in operating distance, scattered light intensity and operator error causing the probe to contact the page.

2 Sample heating

As discussed above, the thermal effects of exposing a manuscript to illumination are often overlooked. Ricciardi et al., in reporting on the use of a thermal imaging camera to determine temperature rises during NIR

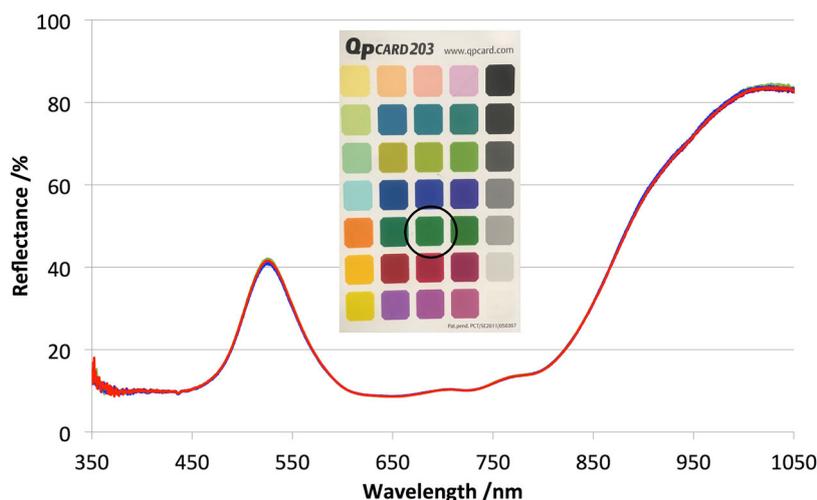


Fig. 6 Four reflectance spectra recorded from different areas of a green panel of the colour standard card (inset, third from left, third up). Each spectrum involved the re-acquisition of a fresh white reference spectrum (Spectralon® tile) and complete realignment of the sample. The difference in reflectance over the range 350–1050nm is $\leq \pm 1\%$. Spectra acquired using $16 \times 100\text{ms}$ acquisitions.



Fig. 7 (a) *left*, Thermal imaging of a sample of carbon black, showing no detectable temperature rise using 'Team Pigment' FORS system, with an illuminance of 2.4mWcm^{-2} $350\text{nm} < \lambda < 1400\text{nm}$, and (b) *right*, under high-power illumination, 150mWcm^{-2} , $350 < \lambda < 2600\text{nm}$, giving a rise of 14°C (from 19.8°C to 33.7°C). In this example the light is imaged from a single $1000\mu\text{m}$ diameter fibre imaged onto the paint surface.

¹⁹ Cf. Ricciardi et al., 'Near Infrared Reflectance Imaging Spectroscopy to Map Paint Binders'.

reflectance measurements, recorded a 1.4°C rise, under poorly specified illumination conditions.¹⁹

For the thermal testing executed in the work here samples made from leaves of vellum and paper were painted with carbon black and azurite in gum Arabic and egg tempera binders and allowed to air dry before being placed at the focus of the FORS probes. A thermal imaging camera was then used to monitor the temperature of the painted areas during illumination.

Using the Team Pigment FORS probe with a water filter placed in the light path and a power density corresponding to 1250lux , ($350 < \lambda < 1400\text{nm}$, 2.4mWcm^{-2}), no discernible rise in temperature could be detected for either the carbon black or the azurite samples on both parchment and paper, even after exposure times in excess of one minute (see Fig. 7a). Increasing the illuminance to $12,500\text{lux}$ ($350 < \lambda < 1400\text{nm}$, 25mWcm^{-2}), gave rise to an increase in temperature of $\approx 0.5^\circ\text{C}$ over a period of 5 seconds for the samples, which can be considered minimal. Extended exposures did not give rise to further temperature rise. When using the full spectral window and high illumination intensities, ($350 < \lambda < 2600\text{nm}$, 50mWcm^{-2}), the illuminated areas of the samples were observed to show more dramatic increases of up to 5°C over a period of a few seconds. Importantly after the illumination was stopped, it took up to 10 seconds for the sample temperature to fall back to the ambient temperature demonstrating the poor heat conduction of the paints on both the parchment and paper substrates.

At still higher power densities, 150mWcm^{-2} , $350\text{nm} < \lambda < 2600\text{nm}$, corresponding to a visible light exposure of approximately $25,000\text{lux}$, a temperature rise of 14°C was observed for a sample of carbon black and a rise of 10°C for azurite painted onto paper (see Fig. 7b). Under this illuminance even plain parchment was observed to increase in temperature by 5°C . Such a level of illuminance could only be obtained using our equipment when the output of the lamp was directed through a 1mm diameter fibre and imaged onto the paint surface, however, we are aware that such power densities can readily be attained using commercial instruments.

Conclusions

We present a low-cost, simple design for a probe that provides excellent spatial and spectral resolution, employing low optical powers: 1250lux and 2.4mWcm^{-2} in the range 350–1400nm, and a safe stand-off from the manuscript surface, which is capable of recording spectra in less than 1 second. The use of two overlapping illumination beams permits precise identification of the sampled area and also provides excellent replication of signal-levels. Further developments incorporating a low-illuminance NIR detection system are under way and will be reported separately at a later date. An alternative system assembled from off-the-shelf components, including a fibre bundle probe, gave good signal levels at acceptable light levels but needed to be held in close proximity to the page. This design proved impossible accurately to reposition for reproducible results, and suffered from fluctuating signal levels.

This work also demonstrates the importance of understanding in detail the spectral profile and powers employed by light sources used in the instrumentation used for FORS measurements. The heating of manuscript samples during FORS measurement has been evaluated: the Team Pigment system causes no detectable rise in temperature of the manuscript surface when operating at a low illuminance of 1250 lux. At low total illuminance powers of $<25\text{mWcm}^{-2}$ there is negligible sample heating, but higher power densities can give rise to a significant localised temperature rise. The judicious filtering of the light sources, particularly in the NIR region, can remove unwanted radiation and significantly reduce the thermal burden placed on the sample. We advocate that power densities should be recorded and published by those employing the FORS method and argue that it is imperative that these densities be reduced to a minimum. The illuminance of FORS spectrometers, whether they be home-made or commercial instruments, should be established and operators must demonstrate that they do not bring about any significant rise in temperature for samples prior to their use.

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Abstract

Fibre-optic reflectance spectroscopy is widely used as a tool for the analysis of coloured materials such as pigments and paints. We describe a new design for a FORS probe which is held some 5cm away from the sample surface and interrogates a spot of 2mm diameter, offering a significant advantage over existing methods. The spectrometer employs an illuminance of 1250lux, equivalent to 0.5mWcm^{-2} averaged across the visible spectrum. The spectral measurements take less than a second ensuring that the risk of

sample photodegradation is minimal. Under these conditions there is no detectable temperature rise of the illuminated area. Increasing the illuminance above 25mWcm^{-2} , a light level significantly higher than that required for our measurements, gave rise to significant localised temperature rises in model manuscripts. This demonstrates the need for caution when using this technique for the analysis of precious heritage items.

Résumé

La spectroscopie de réflectance à fibre optique est largement utilisée comme outil d'analyse des matériaux colorés tels que les pigments et les peintures. Nous décrivons une nouvelle conception d'une sonde FORS qui est tenue à environ 5cm de la surface de l'échantillon et interroge une tache de 2mm de diamètre, offrant un avantage significatif par rapport aux méthodes existantes. Le spectromètre utilise un éclairage de 1250lux, équivalent à $0,5\text{mWcm}^{-2}$ en moyenne dans le spectre visible. Les mesures spectrales nécessitent moins d'une seconde, ce qui garantit que le risque de photodégradation de l'échantillon est minime. Dans ces conditions, il n'y a pas d'élévation de température détectable de la zone éclairée. L'augmentation de l'éclairage

au-dessus de 25mWcm^{-2} , un niveau de lumière significativement supérieur à celui requis pour nos mesures, a donné lieu à des augmentations de température localisées significatives dans les manuscrits modèles. Ceci démontre la nécessaire prudence lors de l'utilisation de cette technique pour l'analyse d'objets patrimoniaux précieux.

Zusammenfassung

Faseroptische Reflektionsspektroskopie (FORS) ist weit verbreitet als ein Werkzeug in der Analyse von farbigem Material wie Pigmenten und Farben. Wir beschreiben eine neue Methode, in der ein FORS Sensor etwa 5cm von der Probenoberfläche entfernt gehalten wird und dabei einen Punkt von 2mm Durchmesser untersucht. Dies bietet große Vorteile im Vergleich zu herkömmlichen Methoden. Das Spektrometer nutzt eine Beleuchtungsstärke von 1250lux, äquivalent zu $0,5\text{mWcm}^{-2}$ gemittelt über das sichtbare Spektrum. Die Messungen brauchen weniger als eine Sekunde und das Risiko der Photodegradation der Probe ist minimal. Unter diesen Konditionen kann in dem beleuchteten Bereich keine Temperaturerhöhung festgestellt werden. Wenn die Beleuchtungsstärke auf über 25mWcm^{-2} erhöht wird, ein Lichtwert, der weit über dem liegt, der für unsere Messungen benötigt wird, liegt, dann konnten auf Modellhandschriften signifikante, lokale Temperaturerhöhungen festgestellt werden. Dies unterstreicht die Notwendigkeit Vorsicht walten zu lassen, wenn diese Methode an wertvollen Kulturgütern zum Einsatz kommt.

Resumen

La espectroscopia refractaria de fibra óptica se utilizada mucho como instrumento de análisis de materiales de color como pigmentos y pinturas. Describimos un nuevo diseño de sonda FORS que se mantiene a unos 5cm de distancia de la superficie de la muestra y analiza una zona de 2mm de diámetro, ofreciendo una ventaja significativa sobre los métodos existentes. El espectrómetro emplea una iluminancia de 1250lux, promediada de todo el espectro visible, equivalente a $0,5\text{mWcm}^{-2}$. El riesgo de foto-degradación de la muestra es mínimo ya que las mediciones espectrales llevan menos de un segundo. Bajo estas condiciones no se detecta aumento de temperatura en el área iluminada. El aumento de la iluminancia por encima de 25mWcm^{-2} , un nivel de luz significativamente más alto que el requerido para nuestras mediciones, causó considerables aumentos de temperatura localizados en los manuscritos modelo. Esta investigación demuestra la necesidad de usar esta técnica con precaución en el análisis de piezas valiosas del patrimonio.

摘要

反射光谱学之于照度的优势

光纤反射光谱技术广泛应用于有色材料（颜料和油漆等）分析。我们将介绍 FORS 探头的一个新设计——它与样品表面保持约 5cm 的距离，探测点直径为 2mm，这与现有其他方法相比具有显著优势。光谱仪采用 1250 勒克斯的照度，相当于整个可见光谱平均值为 $0,5\text{mWcm}^{-2}$ 。光谱测量时间不到一秒钟，这使样品光降解的风险降

到最小。在这些条件下，照明区域没有明显的温度升高。若我们将照度提高到 25mWcm^{-2} 以上（明显高于测量所需的光照水平），便会导致样本手稿局部升温显著。这说明在对珍贵遗产文物使用这种分析技术时需要格外谨慎。

Biographies

Andrew Beeby is a Professor of Chemistry at Durham University with research interests in photochemistry and spectroscopy. He is a founder member of 'Team Pigment', a consortium of scientist historians and conservation scientists applying state-of-the-art, non-invasive and non-damaging spectroscopic techniques to systematically investigate the changes in the use of pigments in manuscripts. Work has included the study of books from the early fifth century through to the fifteenth century, as well as the development of mobile, high-performance instrumentation dedicated to the study of heritage objects.

Louise Garner is a doctoral scholar working in both the history and chemistry departments at Durham University. Funded by the Leverhulme Trust through the Centre for Visual Arts and Cultures, Louise's main area of study involves investigation of non-invasive spectroscopic techniques to analyse the pigments used to create medieval manuscripts so that, once identified, the use of pigments in Medieval Britain and the construction of manuscripts more generally can be further ascertained.

David Howell ACR was appointed Head of Heritage Science at the Bodleian Libraries, Oxford in 2012, having first joined in 2004 as Head of Preventive Conservation, and from 2006 Head of Conservation and Collection Care. He has been in the conservation profession for nearly 30 years and prior to his work at the Bodleian he worked on a number of conservation research projects for Historic Royal Palaces (Hampton Court Palace, Tower of London, Kensington Palace) while at the same time co-establishing Hanwell Monitors, the heritage environmental monitoring system. David has served as a trustee to both the Institute of Conservation and the UK's National Heritage Science Forum.

Catherine Nicholson is a Senior Lecturer of Chemistry at Northumbria University, and a founder member of 'Team Pigment'. Her research expertise in nanomaterial engineering and spectroscopic analysis has branched into non-invasive methods of pigment analysis on artefacts, manuscripts and art. She was awarded a RSC mobility fellowship to pursue this research at the Fitzwilliam Museum in 2014 to investigate pigments used on manuscripts between the seventh and fifteenth centuries, work from which became part of the Fitzwilliam's 2016 bicentenary exhibition, *Colour: The Art and Science of Illuminated Manuscripts*. She has worked on a range of conservation investigations since then in collaboration with Durham University and the Bodleian Libraries.

Materials and suppliers

All optical instrumentation:

Ocean Optics

Whichford House, 1400 John Smith Drive
Oxford OX4 2JY

UK

<https://oceanoptics.com/>

FLIR-One thermal imaging camera:

FLIR Systems UK

2 Kings Hill Avenue, West Malling
Kent ME19 4AQ

UK

<http://www.flir.co.uk/>

QP Card QP Color Reference Card 203:

Pigments from Cornelissen and Kremer Pigmente

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