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# The examination of the Book of Kells using micro-Raman spectroscopy

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**The Book of Kells, Trinity College Dublin MS 58, is one of Ireland's greatest cultural treasures, and as such all aspects of its production have attracted academic attention. Until recently, studies of its dyes and pigments have relied exclusively on techniques such as visual and optical microscopic and spectroscopic examination, and comparison of the appearance of the pigment with specimens prepared using ancient or medieval recipes. These studies have yielded interesting results, but, due to the limitations of the examination techniques, they have remained incomplete and somewhat speculative. This article presents the results of a pigment analysis that took place between 2004 and 2006 using micro-Raman spectroscopy. In total, 681 sites over the 4 volumes of the Book of Kells were analysed using 2 separate laser wavelengths (632.8 and 532 nm), making this the most extensive Raman spectroscopic investigation of a single medieval manuscript. In this article several pigments are identified, in particular, blue (indigo), red–orange (red lead), yellow (orpiment), green (vergaut), black (carbon and iron gall ink), and white (gypsum). In addition, purple (orcein) is also discussed.** 

**Keywords:** Book of Kells; pigments; micro-Raman spectroscopy

## Introduction

The Book of Kells is a large calfskin-parchment manuscript codex, dating from around 800 CE, of the four gospels based on the Vulgate text.[1,2] It contains 340 folios (680 pages), although originally it may have had 370 folios.[1,3] There are 34 full-folio decorated pages featuring symbols and portraits of the Evangelists, Christ, the Virgin and Child, and illustrations of events in the life of Christ. Since 1956, the manuscript has been bound in four volumes, one for each of the gospels: Matthew, Mark, Luke and John.

The Book of Kells has survived as one of the greatest examples of medieval Christian art. It is renowned for the richness of its decoration, which ranges in complexity from full-page compositions based around words, initials and portraits, to small details used to augment and emphasise text.

Despite numerous studies of its history, iconography, materials and techniques, many questions remain about its origins and production, and there have been discrepancies and differences of opinion in published descriptions of the range and type of pigments used by its scribes.

In the past 50 years there have been three major pigment studies. In 1960, Roosen-Runge and Werner examined the manuscript using low-power polarising light microscopy,[4] and by comparing the optical characteristics of the pigments with samples prepared according to medieval recipes. In 1989, Cains[5] reviewed the work of Roosen-Runge and Werner, and re-examined the manuscript using optical microscopy with some differing results. In a more extensive study in 1991–1992, Fuchs and Oltrogge[6] employed colour spectroscopy as well as optical microscopy. While concurring with the previous studies in certain respects, they also proposed some new conclusions.

The three studies had a common difficulty: inadequate access to the manuscript to allow a comprehensive examination to be completed; and the limitation of the non-invasive technologies available for the *in situ* study of the pigments.

The studies identified approximately 28 different pigments along with a number of pigment mixes (Table 1).

The identifications were based on a number of criteria: the optical or spectroscopic characteristics of the pigments; the identification by other researchers of pigments on objects of similar age or type; historical evidence on the availability of the pigments during the medieval period or earlier; and the condition of the pigment, using such criteria as tarnishing, corrosion, gloss, fading and darkening.

The present study of the Book of Kells aims to validate or correct the pigment identifications of previous studies, to investigate further the binding media and support as well as the working methods of the artists, and to record the condition of the manuscript.

The requirements of the study were that all techniques used would provide definite quantitative data. The techniques were to be chosen from those that have been applied with success to the examination of similar objects; and that had been shown to be non-invasive, non-destructive and capable of being carried out *in situ*.

Micro-Raman spectroscopy was selected for an initial exploratory study to identify the pigments due to its well-documented application as a useful technique for the analysis of pigments.[7]

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**Table 1.** List of pigments previously identified

| | |
|---|---|
| Black and brown | Carbon black, iron gall ink, sepia, brown ochre |
| Red | Red lead/minium, red ochre, cinnabar/vermilion, realgar, red folium |
| Pink/purple | Kermes, shellfish purple, organic purple, organic red lake, madder, red folium, purple folium |
| Yellow | Yellow ochre, orpiment, ox gall, yellow lake |
| Green | Verdigris, vergaut, sap green, copper green, malachite |
| Blue | Ultramarine, indigo/woad, blue folium |
| White | Chalk white, lead white |

In this study we have confirmed some of the predominant pigments used on the more richly decorated folios. The results highlight the sophisticated use of a restricted palette of organic and mineral pigments. These have been applied with great creativity, as pure colour and as simple mixtures. Variety has been achieved though considered juxtaposition and simple layering. Although the results are not yet comprehensive, a greater insight into the ingenuity with which the manuscript was created has been achieved.

## Experimental

### Apparatus

Raman spectra were obtained using a HORIBA Jobin Yvon labRAM HR. The bench-top micro-Raman unit has an 800 mm focal length spectrometer giving it a resolution of $<1\ cm^{-1}$. Two laser lines were used, a 632.8 nm HeNe laser and a 532-nm Nd : YAG laser. Spectra were acquired directly from the manuscript using two remote probes (superheads), one for each laser line, coupled to the integrated confocal microscope via fibre optic cable. The signal was collected on a high resolution air-cooled CCD. The spectrometer was calibrated at the beginning and end of each measurement session using a polished, non-oxidised silicon standard.

Each superhead was fitted with a digital camera to allow visual focusing and monitoring for sample damage. Rough-focus was achieved by raising and lowering the superhead on a custom-built holder; this rig allowed the superhead to be moved laterally over the manuscript surface and reduced the need to handle the manuscript during examination. Fine-focus was achieved with a small piezo motor attached to the focusing lens on the superhead and controlled through the Raman software.

A long focal length 50× objective lens was fitted to the superhead, giving a clearance of approximately 8 mm above the manuscript surface. The focused laser spot size measured less than 5 μm in diameter and had an approximate intensity of 2.25 mW. Where possible at least 10 accumulations were taken at each sample site, with total measurement time generally varying between 20 and 60 s. In certain areas, such as regions with worn or noticeably damaged pigment, spectra were gathered over longer intervals of up to 20 min.

In addition to the micro-Raman spectroscopy, false colour infrared (FCI) imaging was carried out on a number of folios using a MuSIS-HG multi-spectral imaging camera from Forth Photonics.

### Reference samples

Collected spectra were matched with Raman spectra standards[8,9] including a spectral library created in-house from samples prepared from dry pigments purchased from Winsor & Newton, Kremer Pigmente, and L. Cornelissen & sons,[10–12] bound in gum Arabic, and painted on to a parchment support.

### Examination set-up

The manuscript was supported throughout the examination periods using foam wedges and polyethylene straps and the examination room was conditioned to match the manuscript's storage and display conditions with the relative humidity set at 50–55%.

Examination sites were chosen according to a number of criteria. All major decorated folios and any with unusual features – such as a palette change or a technical difference from the majority of the decoration – were selected. Special care was taken to match exact sites mentioned in the three previous investigations to allow for direct comparison. An attempt was made to analyse all different pigments, and pigment layers, as well as the different script inks.

## Results and Discussion

In general the HeNe laser, 632.8 nm was the most effective laser line for the range of material measured. Almost half of the results matched Raman spectral standards. As expected, not all pigments were detected satisfactorily using micro-Raman spectroscopy, and further analysis was planned with *in situ* Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray fluorescence (XRF), UV fluorescence and multi-spectral imaging.

### Blue

Commentators have long marvelled at the use of blue in the Book of Kells, and there has been comment that the extensive use of the colour is unusual for insular manuscripts.[13] Three pigments have been proposed: folium, a dye extracted from the plant *Chrozophora tinctoria*; indigo from either the *Indigofera* species or the *Isatis tinctoria* species (woad)[14]; and ultramarine from the mineral lapis lazuli. Ultramarine was identified in the three previous examinations, in combination with glazes, and in layers, and has been mentioned in many scholarly publications about the manuscript.[1,15]

In total, 106 blue sites of varying shades of blue and varying opacity were examined throughout all four volumes. All but four of these sites have been identified as containing indigo (indigoindigotin) $C_{16}H_{10}N_2O_2$ which is characterised by bands at ~550, 604 (Fig. 1) and 1585 $cm^{-1}$ (Fig. 2).[16,17] In two of the four exception cases, points nearby in the same region of pigment yielded spectra indicative of indigo.[16–21] The peak at 1019.5 $cm^{-1}$ is most likely due to the addition of white, which has been attributed to gypsum (Fig. 4)

### Green

In total, 88 sites of green pigment were examined throughout all four volumes with 59 of them giving spectra containing the identifying peaks of both orpiment and indigo. The spectrum for such sites would typically contain peaks at ~297, 315, 359 and 386 $cm^{-1}$ from the orpiment constituent, and peaks at ~550, 604 and 1585 $cm^{-1}$ arising from the indigo component. This mix of colours, known as vergaut, is not uncommon.[19,20,22] (Fig. 2)

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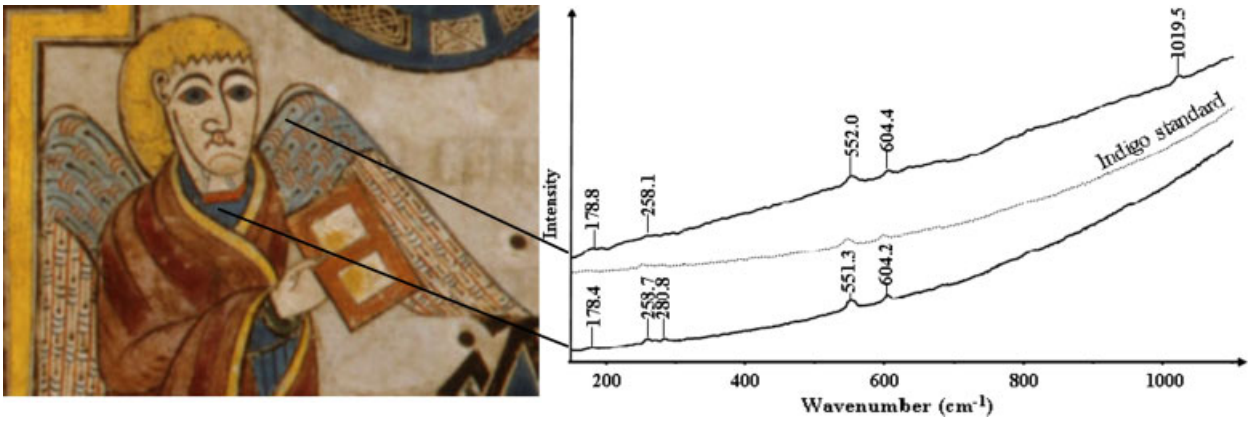


**Figure 1.** The solid lines depict the Raman scan from the wing and shirt of an Angel in the top left corner of folio 183r. The dotted line depicts the Raman scan of an indigo standard. The additional peak at 1019.5 is indicative of gypsum. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

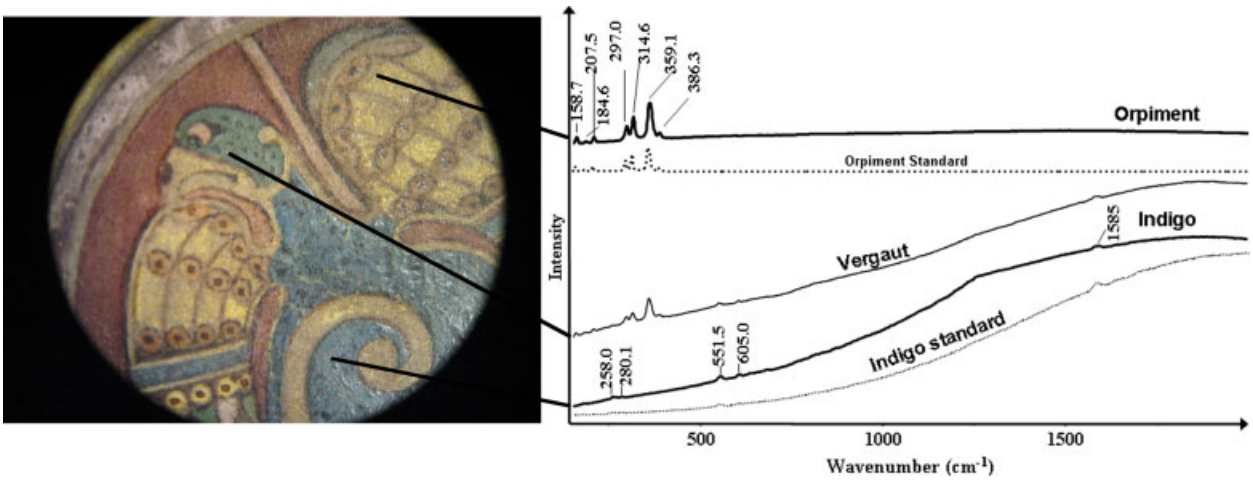


**Figure 2.** Vergaut, orpiment and indigo Raman spectra (solid lines) taken from the head, wing and back of an eagle on folio 129v. As can be seen from the spectra the green pigment in the head of the eagle is a mix of orpiment and indigo known as vergaut. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

The remaining 29 sites were green areas which displayed a bluish green to a bright glassy-green colour with characteristic degradation of the parchment support usually associated with verdigris.[23,24] These sites produced highly fluorescent Raman spectra showing no detail.

### Yellow

A total of 87 sites of yellow pigment were investigated throughout all four volumes. Of these sites, 71 showed the characteristic peaks (297, 315, 359 and 386 $cm^{-1}$) of orpiment (Fig. 2), arsenic(III) sulphide $As_2S_3$ (known as *auripigmentum* or 'yellow gold' in the middle ages).[9,18,20,22,23,25,26] These peaks were consistent with both our pigment standard and several orpiment samples obtained from the Trinity College Geological Museum.

Regions displaying a translucent brown/yellow colour gave fluorescent spectra with no discernible peaks.

### Orange/red

A total of 97 sites of an orange/red colour were investigated throughout all four volumes and 77 of these sites produced the characteristic spectral peak for red lead, lead oxide, $Pb_3O_4$. The main characteristic peak for red lead is at ~550 $cm^{-1}$, and arises from the stretching of the Pb(IV)–O bond.[20,22,26,27] (Fig. 3)

### White

Seventy-four white pigment sites were investigated, with 59 exhibiting peaks between 1015 and 1026 $cm^{-1}$.

This white pigment, used throughout the manuscript, predominantly in the faces and hands of figures, yields Raman spectra with a prominent band either at ~1018 or at ~1024 $cm^{-1}$, which can be attributed to vibration $v_1$ ($a_1$) $SO_4^{2-}$ of two dehydrated forms of gypsum ($CaSO_4 \cdot 2H_2O$), gypsum anhydrite ($CaSO_4$) and bassanite ($CaSO_4 \cdot 0.5H_2O$), respectively.[14]

The presence of bassanite, which has been known to be a metastable compound, suggests a continuing transformation between the hydrated and anhydrite forms. Although it has been shown that bassanite is present as an intermediate step in the transition of gypsum both to and from gypsum anhydrite,[28] further work is needed to model the behaviour of the pigment over long periods of time at room temperature. As parchment is highly hygroscopic, over time it could provide the required moisture for reversion of the anhydrite form to bassanite. Similarly, with the variety of atmospheric and environmental conditions within



  

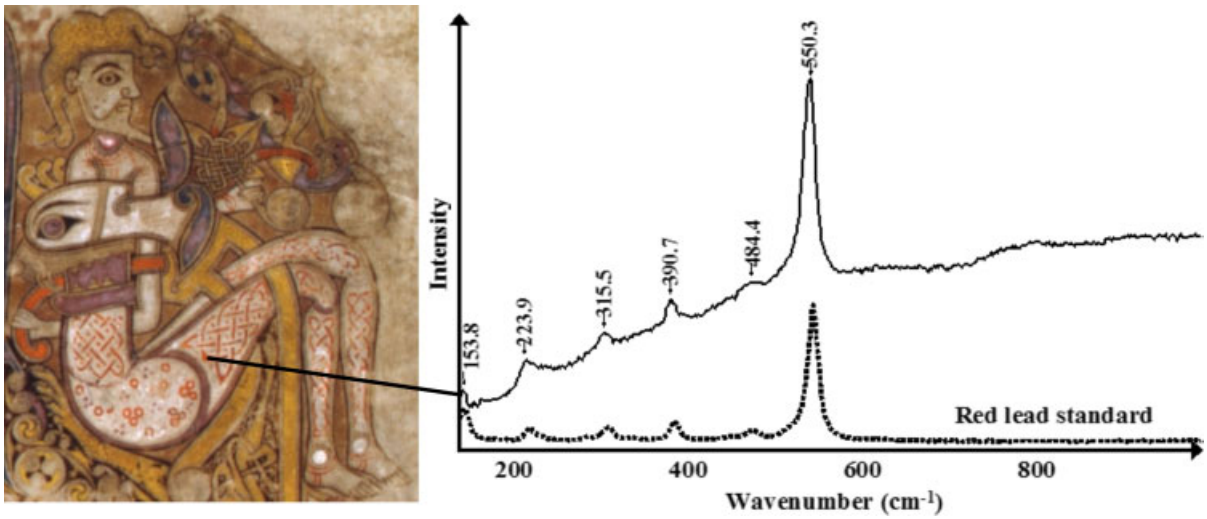


**Figure 3.** Raman spectra showing red lead standard (dotted line) and red lead from the knot work on the leg of a warrior in the topmost right corner of folio 130r. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

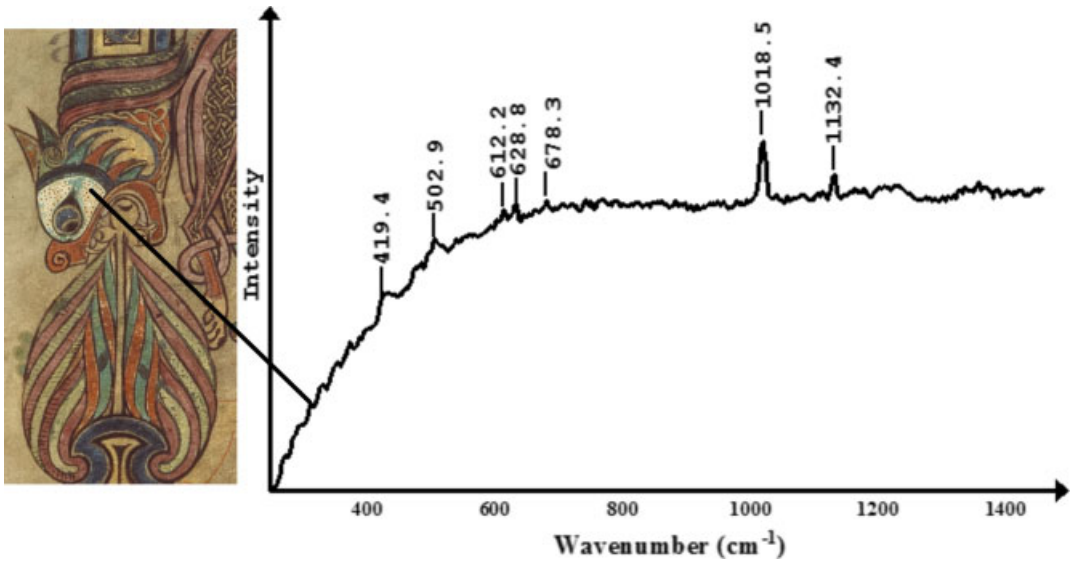


**Figure 4.** Raman scan of the white pigment in the head of lion on the top left of folio 124r. The bands at 419, 503, 629, 678, 1019 and 1132 $cm^{-1}$ are suggestive of gypsum anhydride. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

which the manuscript has been stored over its long history, it is equally possible that the original pigment was the fully hydrated form of gypsum, which then lost its moisture over time.[14]

Some areas of this pigment, which appear on less worn folios, (especially on folios 124r and 185r), show additional peaks at ~503 and 1038 $cm^{-1}$ also associated with dehydrated forms of gypsum.[9,29]

Several sites of light blue and purple also yielded an additional peak suggesting a mixture containing gypsum. In the majority of cases the peak was at ~1018–1020 $cm^{-1}$ suggesting the presence of gypsum anhydrite, but some sites displayed a peak at ~1024 $cm^{-1}$ suggesting the presence of bassanite. On folios with both white sites and blue sites displaying the gypsum derived peaks (such as folios 1r and 2v) the relevant peaks were at the same position on both sites (Fig. 4)

## Black

In total, 63 black sites were investigated throughout the manuscript, 31 of which showed at least one peak representative of a form of carbon. Of these sites, 20 show the broad dual band[29–32] set of 1330 and 1600 $cm^{-1}$ suggestive of amorphous carbon. Sixteen of the sites show a band at ~1480 $cm^{-1}$ (Fig. 5). This Raman peak is similar to that of either amorphous carbon containing some diamond phase carbon[33] or a mix carbon and iron gall.[34,35]

As mentioned above, a significant number of the sites measured did not yield a useful Raman spectrum, instead giving broad fluorescence peaks. In order to augment the Raman study of the black pigments, a representative selection of black pigment sites also examined using FCI imaging. This method uses a series of photographic filters and electronic image stacking to give a final image in which the reflected light from the area of capture is shifted down, i.e. towards the blue end of the spectrum. This

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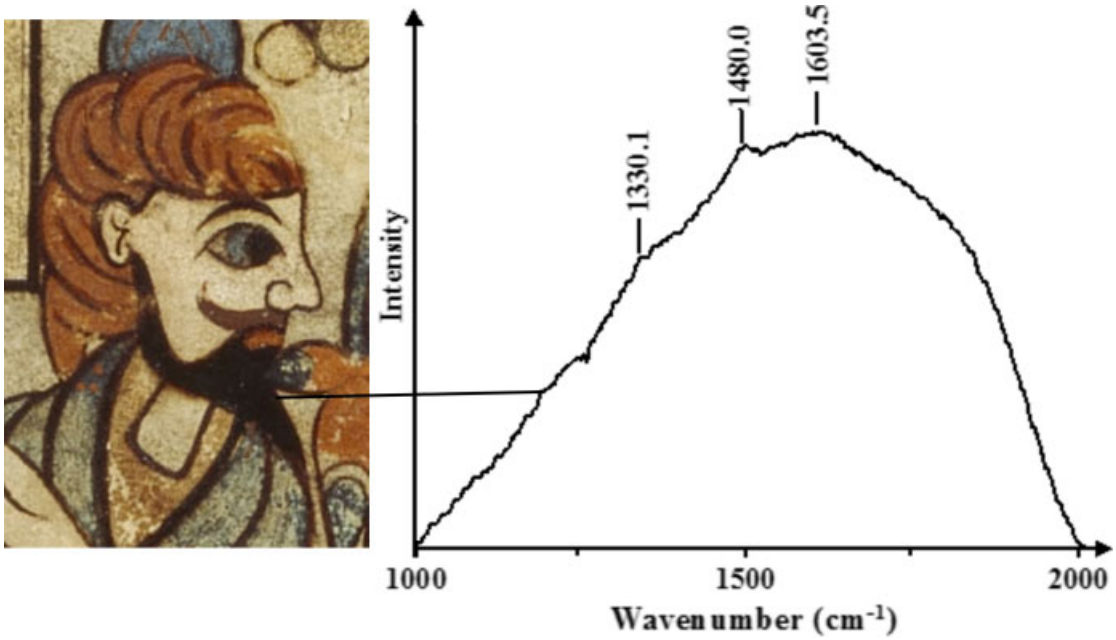


**Figure 5.** The dashed line shows the Raman spectrum of amorphous carbon standard, the solid line depicts the Raman spectrum from the beard of a warrior in the top left of folio 114r. The bands at ~1330 and ~1600 $cm^{-1}$ are seen in the amorphous carbon standard. The band at 1480 $cm^{-1}$ is suggestive of the presence of the diamond like allotrope of carbon. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

allows for a visual representation of the infrared light reflected from the site.

An unpublished in-house investigation showed that when viewed with FCI, carbon black shows no appreciable change in colour; iron gall ink, however, shows a characteristic cherry-red appearance (Fig. 6). Any black ink areas exhibiting this change gave no appreciable change when investigated with Raman spectroscopy, while only those sites that yield no colour change under FCI yielded the Raman spectra with peaks mentioned above.


**Figure 6.** Samples of known pigments (left) shown under ordinary photography (top) and false colour infrared (FCI) (bottom), compared to a sample of text from folio 125v (right), shown under both ordinary photography (top) and FCI (bottom).

### Purple

Purple is found throughout all four volumes of the manuscript. Where it appears as a single layer, Raman spectra were difficult to obtain due to fluorescence effects.[22] On sites where a purple is found as an overlay on either green or blue, however, a distinct set of peaks was measured at ~618, 1179, 1414 and 1639 $cm^{-1}$. This peak combination is not seen on any sites where either blue or green occurs as a single layer. In the cases with the peaks listed above, the underlying pigments have been identified in each case to be either indigo or vergaut, respectively (Fig. 7).

While the Raman spectra for these purple pigments do show some similarities with Tyrian purple,[36] recent investigation of the purple areas on the Book of Kells by MOLAB (University of Perugia), using luminescence lifetime measurements, has indicated that the pigment is orcein $C_{28}H_{24}N_2O_7$, a dye produced from the lichen *Roccella tinctoria*.[14,37]

## Conclusions

The result of this initial study has been to confirm the extensive use of five pigments (red lead, orpiment, indigo, gypsum, carbon black and iron gall ink); and the identification of several simple mixtures, including orpiment and indigo (vergaut), gypsum and indigo, and a gypsum and purple mix.

Thus far results indicate a simple palette that could be created from sources reasonably local to the sites where the manuscript is thought to have originated.[1]

This study does not represent a complete identification of all pigments used for the Book of Kells. For example, pink and a translucent yellow/brown remain unknown. The limitation of Raman spectroscopy is that not all compounds are Raman active, while others fluoresce under the laser light illumination in such a way as to drown out any Raman signal that might be present. There are several folios with a distinctive and different pigment palette to the rest of the manuscript, containing 'earthy' pigments in brown, orange and green tones, such as folio 28v, from which no useful Raman spectra could be extracted.

Further research is being undertaken as a result, including a study of all pigments with a battery of complementary characterisation techniques such as FTIR and XRF spectroscopy, to provide conclusive results on those pigments that proved inscrutable to micro-Raman spectroscopy. Two other pigment-



  

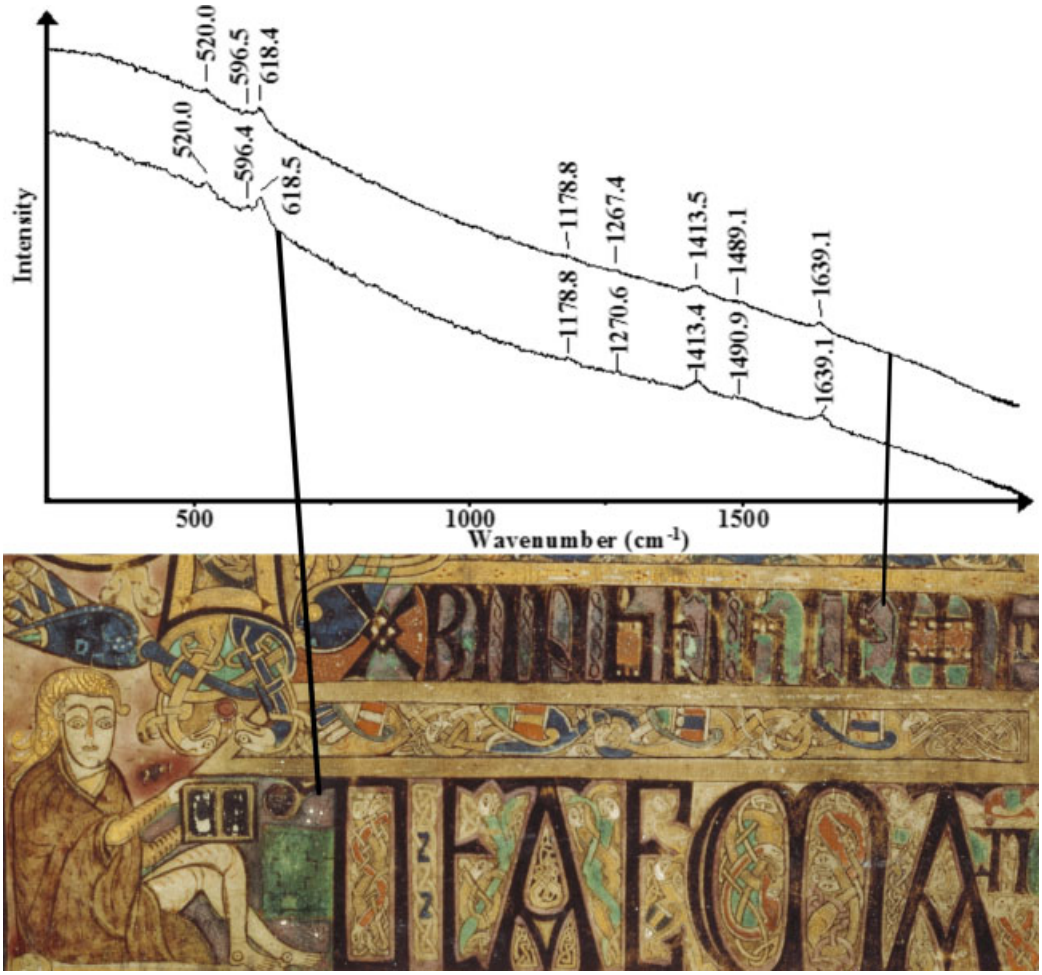


**Figure 7.** Purple spectra from two sites in the large lettering in the middle of folio 8r. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

specific studies also present themselves: a study of the nature of the gypsum-based pigment and further study of the orcein purple. Research is currently in progress in both of these areas.

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