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The Book of Uí Mhaine: An Interdisciplinary Analysis of the Materiality of the Gaelic Manuscript Tradition

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Abstract: This paper presents the findings of the first multi-analytical investigation of the Book of Uí Mhaine, one of the largest Gaelic Books surviving from the medieval vernacular period. A combination of protein analysis, point X-ray fluorescence spectroscopy (XRF), multispectral imaging (MSI), point Fiber-Optic Reflectance Spectroscopy (FORS) and point Raman spectroscopy was used to perform a systematic investigation of the Book of Uí Mhaine's constituent materials, including parchment, inks and pigments. The analysis revealed that the parchment was made of calfskin, both blunt tools and Pb-containing materials were used for ruling the pages throughout the manuscript, and iron-based inks were used to write the content of the book. The decoration was restricted to the initial letters and rubrication across the body text. The decoration color palette was limited to yellow and red, comprising arsenic-, mercury- and lead-based pigments. A copper-based green pigment was found only on one folio. The scientific knowledge acquired through this multi-analytical approach complemented a substantial corpus of knowledge already built by Gaelic scholars, paleographers, codicologists and conservators. This work not only allowed for the consolidation of existing information on methods and materials used for the production of medieval Gaelic manuscripts but also laid the basis for future comparative work with other contemporary traditions in Ireland and Europe.

Keywords: proteomic analysis; inks; pigments; X-ray fluorescence; multispectral imaging; fiber-optic reflectance spectroscopy



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1. Introduction

Among an estimated three hundred surviving vernacular Gaelic vellum manuscripts, the Book of Uí Mhaine (Leabhar Ua Maine: Royal Irish Academy MS D ii 1) is one of the most important examples of late medieval Irish books. The Book of Uí Mhaine is a large (42 × 26.5 cm) manuscript written towards the end of the fourteenth century. It derives its name from the ancient tribal area of Uí Mhaine in east Co. Galway and south Co. Roscommon in Connacht. Today, the book consists of 157 leaves, estimated to be less than half of its original size [1]. The contents comprise a collection of traditional Irish learning in the form of genealogies, prose-tales and poetry. Ten different scribal contributions, divided across twenty-five quires, have been identified through paleographic investigation [2]. Because of its large size, scope, extent, and variety of contents, the Book of Uí Mhaine is considered one of the most outstanding productions of Irish scholarship in the vernacular tradition.

A number of analytical techniques are routinely used for the material investigation of medieval books. For example, multispectral imaging (MSI) is widely used to enhance the readability of ancient texts. MSI is also the technique of choice for rapid and non-invasive initial assessment of manuscripts, which is crucial to inform and direct the application of complementary analytical techniques [3–6]. X-ray Fluorescence spectroscopy (XRF) has been shown to be diagnostic for the identification of the elemental content of both pigments and writing inks, often in conjunction with further data processing such as fingerprinting analysis or principal component analysis [7–9]. Fiber-optic reflectance spectroscopy (FORS) is an invaluable method for the identification of organic and inorganic pigments and inks [10–14]. Recently, proteomic analysis has also emerged as a powerful tool for the non-invasive investigation of parchment origins in medieval manuscripts. For example, Fiddymment et al. have used proteomic approaches to reveal the animal origins of parchments used for the making of 13th-century bibles across Europe [15–17]. Additionally, Toniolo et al. have used protein analysis to analyze the making of a pocket bible donated by a Franciscan friar to the Chinese Mogul Emperor in the 13th century [18].

In contrast to mono-analytical approaches, the combined application of multi-analytical techniques has recently gained popularity, whereby elemental, molecular and imaging techniques are used in combination to gain a complete picture of the materials and methods used by ancient parchment producers, scribes and decorators. For example, Ricciardi et al. effectively applied imaging spectroscopy and in situ analytical methods for the identification of materials in a 15th-century illuminated manuscript [13]. Cucci et al. have used a combination of hyperspectral imaging, FORS and XRF to investigate the attribution of the Corale 43 manuscript to Beato Angelico [19]; de Viguerie et al. have investigated 15th-century illuminated manuscripts by a combination of XRF and hyperspectral imaging [20]; whereas Calá et al. used a combination of UV-Vis diffuse reflectance spectroscopy, XRF, optical microscopy and protein mass spectrometry to build a holistic picture of the 14th-century Messale Rosselli [21]. In spite of the large availability of multi-analytical approaches, up until now, Gaelic manuscripts have been investigated only at the macro-level, through the codicological and paleographic investigation of used materials and marking events. The information gathered from such investigations, together with other available historical information, has contributed to building a corpus of data on the choice and availability of materials and on processes used for the manufacture of parchment and ink. Some questions on Gaelic medieval book manufacturing remained open, however, such as the choice of animal species used for parchment production, the processes employed to obtain the parchment folios, the types of ruling techniques, and the nature and origin of constituent inks and pigments. The aim of this work was to carry out a multi-analytical study of the materiality of a representative Gaelic vellum manuscript for the first time in order to gain a better understanding of how manuscripts of the vernacular tradition were written and constructed. The choice of analytical methods was determined by the requirement for minimally invasive analysis. Therefore, MSI, FORS, XRF and optical microscopy were the techniques used more extensively throughout the book. Mass spectrometry-based protein analysis was performed using eraser crumbs collected with conventional PVC erasers. Raman spectroscopy was only used on two microfragments discovered loose on the page or in the gutter of the book during analysis.

2. Materials and Methods

Biomolecular Sampling (Proteins). Twenty-three samples were extracted using the kits sent by one of the authors (Sarah Fiddymment, University of Cambridge), according to a method described elsewhere [15]. Sample collection was undertaken on areas of the manuscript that had no writing and presented structural integrity. All the samples were stored at room temperature until required.

Biomolecular analysis. Protein mass spectrometry (ZooMS) was performed as already described in detail in reference [15]. Briefly, in order to collect collagen, collected eraser samples were centrifuged and solubilized in 0.05 M NH_3CO_3 (AmBic) buffer (pH 8)

and 1 μL of trypsin (0.4 $\mu\text{g}/\mu\text{L}$) and incubated at 37 $^{\circ}\text{C}$ for 4 h. Samples were then centrifuged for 1 min, and 1 μL of 5% (v/v) TFA was added, followed by desalting and a concentration step in C18 resin (Millipore). Eluted peptides were mixed on a ground steel plate with 1 μL of α -cyano-4-hydroxycinnamic acid matrix solution [1% in 50% ACN/0.1% TFA ($v/v/v$)] and air-dried. Extracted peptides from the 23 samples were analyzed using a calibrated Ultraflex III (NLD1; Bruker Daltonics) MALDI-TOF instrument in reflector mode in 3 technical replicates. Spectral analysis was performed using the open-source cross-platform software mMass (www.mmass.org, accessed on 26 October 2022) [22], and individual peptides were identified manually according to Buckley et al. [23,24]. A FAM411 3 T-FV2W model microscope was used to acquire digital images at 50 $\times$ and 200 $\times$ magnification ratios. The instrument was equipped with visible LED lights and a digital camera with 1.3 Megapixel resolution.

Multispectral imaging was conducted using a Megavision system equipped with a 39-megapixel monochrome E6 camera (Kodak) with a CCD sensor (7216 $\times$ 5412 pixel array and a linear dimension of 6.8 microns). Illumination was provided by narrowband (FWHM between 6 and 20 nm) light-emitting diodes (LED) at 365, 400, 420, 450, 470, 505, 530, 560, 590, 615, 630, 655, 735, 850, and 940 nanometers (nm). Megavision, a hyperspectral lens having a focal length of 120 mm and a f-number of 4.5, color corrected from 350 to 1000 nm, was used and operated with an aperture of F11. The exposure times of the camera were adjusted for each narrow-band LED light via calibration to an in-scene Spectralon 99% diffuse white standard. Each capture is flat-fielded to correct for non-uniform illumination and variations of the lens and camera back. The exposure times of the camera were adjusted for each narrow-band LED light to ensure that the full dynamic range of the camera was used. Each capture is flat-fielded to correct for non-uniform illumination and variations in the lens throughput over the field of view. Files were captured as digital negative graphics (DNG), corrected for uniformity or artefacts using a flat fielding technique, and converted into 16-bit tagged image file format (TIFF) files. An X-rite color checker and Spectralon were used as reference standards. Image processing derived from multispectral image cubes was completed in the form of infrared false color (IRFC), substituting the red channel of the visible with the IR image at 940 nm, and principal component analysis (PCA). PCA images were obtained by processing all 15 MSI images.

X-ray fluorescence spectroscopy was performed with a portable, energy-dispersive XRF ELIO (XGLab, srl). The spectrometer was equipped with a Peltier-cooled Silicon Drift Detector with a resolution of 135 eV at the manganese (Mn) $K\alpha$ line (5.9 keV). The excitation source was a low-power (4 W, 50 kV) transmission X-ray tube with a Rh anode. Measurements were performed with no filter under an air atmosphere in a range of 1–30 kV with a tube current of 130 μA . A collimator, allowing a ~ 1 mm-diameter focused spot size on the surface of the folio, was used to acquire XRF spectra. The distance from the folio was ~ 1 cm, and the acquisition time was 240 secs for representative spectra. A semi-quantitative approach to the XRF data was performed using the open-source software PyMca. The so-called fundamental parameter method (FPM) allowed estimating elemental concentrations based on observed peak intensities.

Raman spectra were taken with a Renishaw inVia Qontor Raman Spectrometer System equipped with a 785 nm laser with 300 mW laser power. For the spectra acquisition, 10% power was used to obtain maximum signal-to-noise ratio while avoiding laser-induced damage to the material. The collected polychromatic light was diffracted by 1800 lines/mm grating into its constituent wavelengths and captured on a Peltier-cooled (-70 $^{\circ}\text{C}$) near-infrared enhanced, deep depletion CCD (1024 $\times$ 256 pixels). Spectra were obtained using $\times 100$ objective (0.6 μm spot size)—30 accumulations of 30 s. Spectra were processed in Wire 5.5 using minimal smoothing, cosmic ray removal and baseline subtraction. Deconvolution uses Wire 5.5. mixed Gaussian/Lorentzian curves to identify relevant peaks. Additional Raman analyses were performed using a Renishaw InVia Raman system outfitted with a Leica DM2500 microscope, CCD detector, and Rayleigh edge filters. The laser excitation was 785 nm, and the grating was 1200 L/mm. Exposures ranged from 10 to 100 s at 0.45

or 0.24 mW power, using a 50× or 20× objective. Both instruments were calibrated to the 520.5 cm⁻¹ line of Silicon. Reference Raman spectra for comparison were found on the IRUG website (www.irug.org, accessed on 23 January 2023).

FORS spectra were collected with an ASD FieldSpec 4 from 350 nm to 2500 nm with a collection area of ~3 mm. Spectral resolution is 3 nm at 700 nm and 8 nm at 1400 and 2100 nm. Ten spectra were averaged with a total acquisition time of <5 s. Reflectance was calibrated to a Spectralon 99% diffuse white standard (calibrated every 20 min during data capture). The bifurcated probe uses a halogen light source with a bulb temperature of 2900 K and a spot size of 10 mm.

3. Results

In order to conduct a systematic investigation of the constituent materials, the Book of Uí Mhaine's main features were classified as shown in Figure 1.



Figure 1. Representative photographic images of the Book of Uí Mhaine's analyzed features: (a) Entire page of the book, folio 50 r; (b) Rubricated initial, folio 48 r; (c) Display and main text, folio 49 r; (d) Pricking marks, folio 2 r; (e) Graphic ruling, folio 88 v.

Specifically, Figure 1a shows a representative folio, displaying written text and decorated initials on the vellum support. Figure 1b shows the largest and most outstanding example of a decorated initial letter in the manuscript, colored in red and yellow pigments, indicating the beginning of a new quire. Figure 1c shows an example of the large-format lettering, called display text, typically found at the beginning of a new section of the content. An example of pricking marks puncturing the parchment folios found in the margins of some pages is shown in Figure 1d. The pricking method is used to demarcate the position of the guidelines. Ruling lines, known as guidelines, were drawn on each page in order to guide the writing of the manuscript. Examples are shown in Figure 1e. The details of the Book of Uí Mhaine's structure and the division of hands by scribe, quire, and folio are reported in Table S1 in the Supplementary Materials. All the parts of the Book of Uí Mhaine listed above were analyzed by a combination of different analytical techniques. Specifically, the parchment was examined by a combination of protein analysis, MSI and XRF; ruling was analyzed by MSI and XRF; writing inks, including inks used for the writing of the main text, display text, marginalia and initial letters, were examined by MSI and XRF; pigments were examined by MSI, XRF, and FORS. Raman spectroscopy was performed on micro-fragments of ink and red pigment discovered loose on the page during the visual assessment. Microscopy and photographic images were taken throughout the book to support the findings.

3.1. Parchment

As a first approach to the analysis of the parchment, MSI imaging was used throughout the manuscript to capture characteristics at full-page magnification scale. An example is shown in Figure 2a, where a reflectance image at 365 nm of folio 55 r clearly displays water stain damage appearing as dark areas over a light gray background. The origin of the dark appearance of water-damaged areas under UV illumination is still under debate.

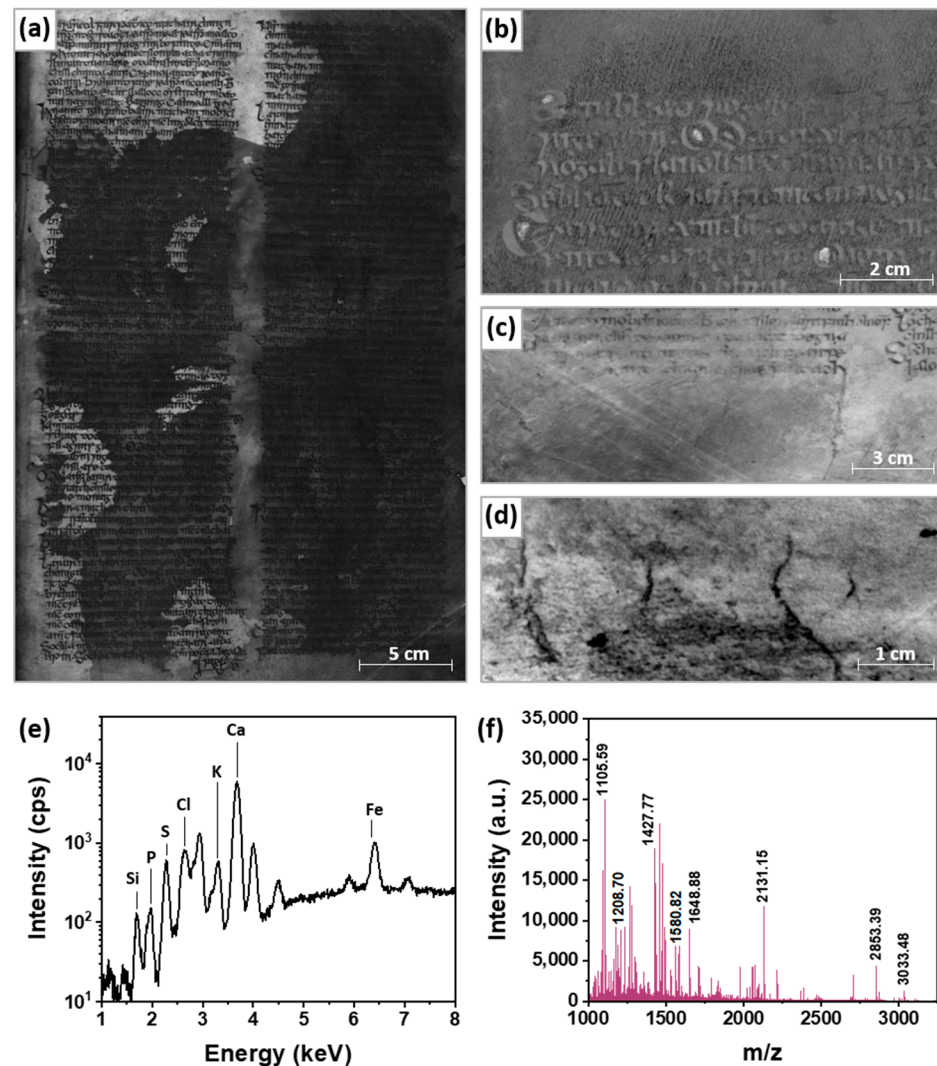


Figure 2. (a) UV reflectance image (365 nm) of folio 55 r showing staining caused by dampness or water; (b) PCA projection of a detail of folio 48 v enhancing scrape marks; (c) PCA projection of a detail of folio 53 v enhancing page folds; (d) IR image (940 nm) detail of folio 50 r enhancing animal veins; (e) Representative XRF spectrum of parchment taken in folio 38 v; (f) Representative MALDI-TOF mass spectrum taken in folio 1 v.

The availability of page-by-page images from the MSI analysis allowed the identification of peculiar water stains across the book. In particular, it was possible to group similarly shaped water stains and identify discrepancies in the current binding order of the quires. For example, a break in similarly shaped water stains was observed between folio 18 v and folio 19 r, corresponding to the transition from quire 4 to 5 (Figure S1 in Supplementary Materials). This break is likely the result of the loss of a single folio at this point. In contrast, continuity of stain marks was observed from folio 47 v to 48 r, marking the transition from quire 9 to 10 (Figure S2 in Supplementary Materials). This might be an indication that these two quires were housed together in a very similar environment even before they were bound together. This aligns with the fact that the Book Uí Mhaine was in

a disbound state until the 19th century. It also confirms the known historical connection between the scribes of quires 9 and 10: quire 9, written by Adam Cusin (scribe C), contains a copy of a poem by the scribe of quire 10, Faelán Mac an Ghabann na Scéal (Scribe F).

The MSI data collected were processed and subjected to Principal Component Analysis (PCA) as required in order to highlight different features of the Book and select areas for further analysis. The use of this procedure facilitated better visualization of the scrape marks left on the parchment during the manufacturing process, consistent with the scraping phase observed and reported to be typical of all manuscripts made from skin. This process involved manually removing the flesh and hair after soaking the skin in a lime bath or an organic solution [25]. The scrape marks, caused by the use of rounded knives, appeared in Figure 2b as diagonal parallel lines in the background of the text. Page folds were also visible in Figure 2c, indicating the events the book underwent after its production. These lines emerged from the background parchment; they intersected at similar locations, usually in the corners of the folios. MSI imaging also provided enhanced visualization of parchment veins, suggesting the preferential use of skins from young animals. In younger animals, the vein trails remain more visible due to less-developed skin layers [26]. Figure 2d shows veins as thin, dark trails against a clearer background. A comprehensive visual and microscopy analysis was conducted on the veins within the parchment. The observed findings lead to the most plausible conclusion that the deposition of dust and dirt primarily occurs on collapsed veins. This alignment between dirt deposition and the vein structures may contribute to the dark appearance under IR illumination. The use of juvenile animals was confirmed by protein analyses of 23 samples collected across the entire length of the book, which revealed that parchment folios were constituted by calf (young *bos taurus*) skin (see Figure 2f). The ability to identify the skin's physical features displayed by MSI analysis is based on the comparison with modern skins, where these features are not obscured by content on the page, ageing or events that adversely affect their clarity. Discussions with parchment makers and practical exercises in parchment manufacture also hone observation skills. XRF was used to complement the information gained by protein analysis with the elemental composition of the parchment folios. In order to avoid contamination from the parts containing ink, XRF measurements were taken from the margins. A representative parchment XRF spectrum is shown in Figure 2e and was characterized by the presence of silicon (Si), phosphorus (P), sulphur (S), chlorine (Cl), potassium (K), calcium (Ca) and iron (Fe). The intense Ca peaks, ubiquitous in all analyzed areas, supported the use of a lime (calcium hydroxide, $\text{Ca}(\text{OH})_2$) solution for the dehairing process of the pelts. Ca is ascribable either to the presence of calcite (calcium carbonate, CaCO_3), as with time $\text{Ca}(\text{OH})_2$ becomes CaCO_3 , due to reaction with atmospheric CO_2 , or is to be attributed to the use of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) for surface smoothing, which would also explain the presence of S. It is known that parchment was rubbed with gypsum to avoid the inks bleeding and being absorbed onto the parchment surface and to give it a silky appearance [27]. The presence of K may indicate the use of some form of alum, K-Al-CO_3 (or K-CO_3), as an abrasive or whitening agent used in the curing of the skin. It is known that some skins were desiccated using either sodium or potassium chloride and the pH was adjusted by treating with ammonium chloride or sulphate with lime and applying potash alum [28]. Accordingly, chlorine (Cl), also omnipresent, was ascribed to the treatments above and/or to the practice of using salt for the preservation of the hides from biological attack [29]. Si may be indicative of the use of pumice powder (high in silicon dioxide, SiO_2) for rubbing the flesh side of the skin [30] or may arise from dirt deposition caused by ageing. Trace quantities of mercury (Hg), arsenic (As), and lead (Pb) were also found and were ascribed to humidity-induced dissolutions and migration of the constituent ruled lines and pigments. Traces of copper (Cu) and zinc (Zn) were also detected in all parchment folios. However, due to their low concentrations and similar intensities found in both the clean parchment and inked areas, it was challenging to determine their specific origin—whether they originated from the parchment or the ink. Hg, As, Pb, Cu, and Zn were particularly evident in the XRF spectra taken from heavily water-damaged

folios. These elements, not related to parchment content, were found to be particularly high in intensity, and evidence of ink transfer from one page to another was observed (See Figures S3 and S4 in Supplementary Materials).

3.2. Ruling

Before the writing phase, the parchment folios were ruled to ensure consistent horizontal and vertical alignment for the written content in each line. During medieval times, guidelines and bounding lines were commonly created through the methods of wet- or dry-ruling. Wet ruling involved the use of inks to trace the lines on the parchment. Dry-ruling, on the other hand, encompassed two techniques: inscribing graphic lines or indenting the parchment with a blunt tool. The graphic line technique involved the use of a lead or silver stylus to create the ruling lines. In such cases, identifiable traces were left on the folio, which would be detected through XRF analysis. Alternatively, a linear indentation was made on the parchment using a blunt stylus, typically crafted from wood or bone. In this second scenario, no detectable elemental traces would be discernible through XRF analysis. A page-by-page visual assessment of the Book Uí Mhaine showed that the ruling practice varied across the book. The majority of the manuscript was ruled in a two-column format. The gatherings written by the scribes G1 and G2, assigned to genealogies, were usually laid out in a multi-column format, the most common style for lists. The nature of the ruling lines was investigated by microscopy, MSI and XRF. Two representative examples of guidelines are shown in Figure 3.

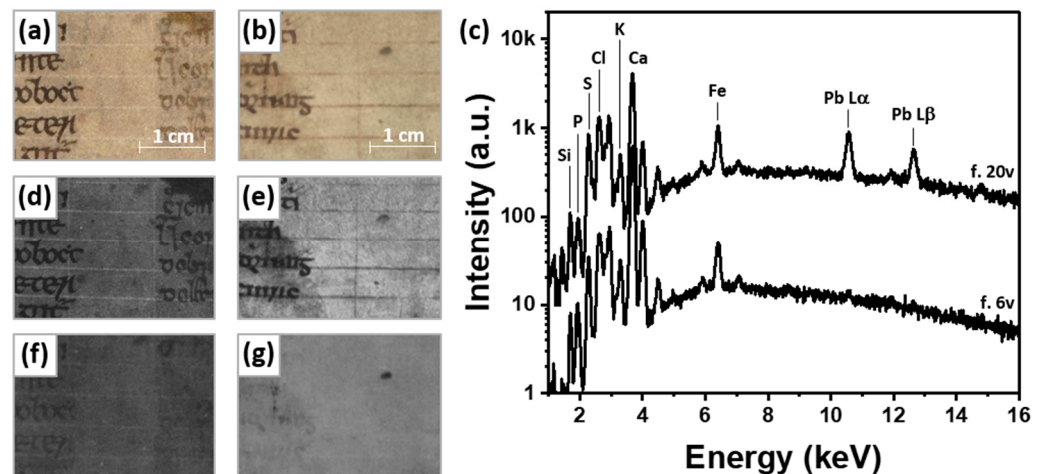


Figure 3. (a) Photograph, (d) UV (365 nm), and (f) IR (940 nm) of dry-ruling, detail of f. 6 v; (b) Photograph, (e) UV (365 nm), and (g) IR (940 nm) of lead-pin ruling, detail of f. 20 v; (c) XRF spectra of lead-pin ruling (top, f. 20 v), and dry-ruling (bottom, f. 6 v).

Folio 6 v exhibited distinctive white underlining lines (Figure 3a), characterized by a groove-like appearance. Under UV and IR illumination (Figure 3d,f), these lines appeared bright on a dark background. In contrast, folio 20v showcased dark graphic lines under both visible and UV illumination (Figure 3b,e). However, these lines vanished under IR illumination (Figure 3g). Studies on drawing media suggest that lines made using a silver-based metal point disappear at 940 nm IR, while lead-based media remains visible at that wavelength [31,32]. To investigate the ruling lines throughout the book, ten areas with varying shades from whitish to gray were subjected to elemental characterization. The spectra analysis revealed the presence of Si, P, S, Cl, K, Ca, and Fe in all areas, attributed to the parchment composition in the background. As anticipated, the indented lines (of a whitish color under visible light) did not exhibit any elemental variation from the parchment. On the other hand, lead (Pb) was detected in the spectra of the graphic lines that appeared dark under visible and UV light and disappeared under IR illumination, while silver (Ag) was not present. The intensity of the Pb peak varied depending on the thickness

of the line, suggesting the use of a Pb-based tool or a Pb-containing ink for creating these dark markings.

Microscopic examination of these areas (See Figure S5 in Supplementary Materials) uncovered physical characteristics such as the presence of what appears to be ink infiltrating between the skin fibrils, suggesting that the material may have been applied in a wet state. In the case of a dry application using a lead-based stylus, it would be expected that the material would adhere to the texture created by the fibrils, remaining on the surface of the rough skin without staining the background. Based on the XRF data, we can preliminarily state that both blunt (wood/bone?) and Pb-containing materials were used throughout the book. However, no discernible correlation was found between these ruling techniques and the contributions of the scribes. For instance, Adam Cusin, the primary scribe of the book, predominantly utilized Pb-based graphic lines in the early quires but more consistently employed a blunt tool in later gatherings. However, folio 45 v displayed a combination of both Pb and indentation rulings.

3.3. Writing Inks

An extensive investigation of the writing inks was performed by MSI, also using infrared false-color imaging (IRFC) and PCA image processing, in order to broadly identify the inks and assess the congruency across the various letter types: body text, display text, and large and small initial letters. The ink used in the main text (Figure 4a) displayed a dark brown hue under visible illumination, which appeared as red coloration in IRFC images (Figure 4b), a behavior usually associated with the presence of iron-based inks [33].

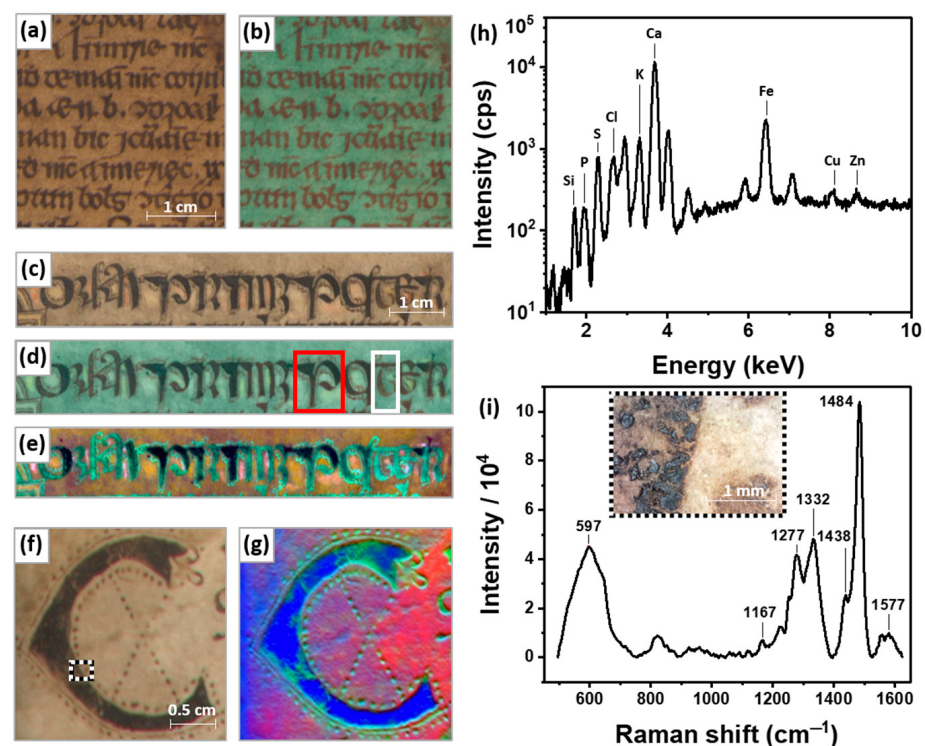


Figure 4. (a) Visible image and (b) IRFC image of a detail of folio 2 r showing body text; (c) Visible image, (d) IRFC image, and (e) Color composite image, based on PCA projections, of a detail of folio 48 r showing display text. Red box highlights a thick application of ink, while the white box highlights a thin application of ink; (f) Visible image; and (g) PCA image of a detail of folio 35 r showing the initial letter C. Dashed box highlights location of inset of (i); (h) Representative XRF spectrum of text ink, folio 2 r; (i) Raman spectrum of the letter body fragment taken at 785 nm. Inset shows an optical microscopy image of the area where the fragment dislodged.

The slight variation between the alignments of the written parts on either side of the folio offered the best areas for XRF analysis, clean from any other material applied on the other side. Although only one representative XRF spectrum of the text ink is shown in Figure 4h, all writing inks, including main text, display text, and initial letters, were found to have similar elemental compositions. The inks are mainly composed of Fe and S, with variable and small traces of Cu and Zn. Cu and Zn are usually associated with iron sulfate used in reaction with polyphenols to obtain an iron-based ink. However, as stated already, these elements are also detected in the writing support. Hence, a thorough quantitative analysis was performed on both the ink (150 spots) and parchment XRF spectra (81 spots). A similar content of Cu and Zn was found in clear parchment and inked areas.

As a result, it cannot be definitively concluded that Cu and Zn are exclusively attributed to the ink. Potassium (K) was ubiquitously present in inked areas at higher intensities than in clean parchment areas nearby, representing either a contribution from the binder (not analysed in this study) or an impurity in the iron compounds themselves [34,35].

Close observation of the MSI images revealed dishomogeneities in the appearance of the ink. This is shown by the display text images of Figure 4c–e, where individual letters displayed different hues of brown in the visible image, appearing as red and black or green and black in the IRFC and PCA images, respectively. The variation in color was ascribed to the different thicknesses of the ink application, with thicker deposition resulting in darker coloration. For example, it was noticed that the darker colors were often located on the serifs, which are an embellishment of the main strokes of the letter, corresponding to thicker applications. Thicker ink depositions would be more resistant to ageing, including abrasion and consequent fading in color. Although the persistence of a dark coloration in the IRFC image could potentially be linked to the presence of carbon (C) in the ink, this point could not be definitively proven during this investigation. Furthermore, it was observed that in laboratory-made samples, thick applications of iron-based ink were not completely transparent to IR (940 nm). A detailed analysis was also performed on selected large initials, which showed similar interesting characteristics, as shown in Figure 4f. Here, the letter “C” in folio 35 r was decorated with internal and external dots, following the shape of the C, all displaying the same brownish coloration. The optical microscopy image, inset of Figure 4i, showed a textured, thick application of dark material in the filling of the letter body, with a degradation pattern of cracking and flaking off the page. Similar to what has been observed for the display text, the assigned green and blue false colors in the PCA image (Figure 4g) suggest the presence of either one thicker application or various depositions of ink to thicken the letter body. In order to shed further light on the nature of used inks, Raman analysis was performed on a dislodged microsample from the body of the letter C. The spectrum recorded at 785 nm showed bands indicative of the presence of iron-based ink (Figure 4i). Specifically, Raman signature bands of iron-based ink were found at 1577 (broad), 1484 (strong), 1438 (shoulder), 1332 (broad) and 550–650 (broad) cm^{-1} , in agreement with literature data [36]. Intense peaks were observed in the 1200–1500 cm^{-1} region, corresponding to the major tannic acid vibrations. The spectrum also showed the shifting of the typical 1477 cm^{-1} band to 1484 cm^{-1} , possibly associated with the presence of other tannins in the ink other than gallotannin. Specifically, the presence of peaks at 1167 and 1277 cm^{-1} could be interpreted as lignin polyphenols and expected to be by-products of tannin extractions, especially if oak galls were substituted with other plant barks [37].

3.4. Pigments

Two main colors were used throughout the book: red and yellow, albeit in different shades. Green in different hues was only used in one instance, for the decoration of folio 111 r.

Red rubrication was widely used throughout the manuscript for the decoration of large capital letters, initial letters and text in the genealogies. Visual inspection of such rubrication across the book revealed the presence of different shades of red, ranging from purple, dark red, orange-red, pink and metallic-lustrous gray with red particles visible to the naked eye. Therefore, XRF was performed on a number of representative red pigmentations

to obtain insight into the nature of these colorations and their various ageing patterns. MSI imaging was performed in conjunction with XRF in order to extend and attribute the XRF data to the folios that were not elementally characterized. A red-orange pigment was used in quires 1, 2, 9, 10, 11, 12, 13, 15, and 16. The elemental composition of that pigment is shown in the XRF spectrum of Figure 5a and was characterized by prominent peaks for mercury (Hg) and sulphur (S), indicative of the use of cinnabar or synthetic vermilion (mercury sulfide, HgS). Arsenic (As) peaks were also detected and interpreted as indicative of the presence of an arsenic sulfide, either realgar, pararealgar, or orpiment. The presence of Pb, which exhibits a main peak ($L\alpha$) that overlaps with As $K\alpha$, was excluded by considering the absence of its corresponding secondary peaks in the analysis. The red area in folio 48 r responded as yellow in IRFC (see insets of Figure 5a), further confirming the presence of vermilion as reported in the literature. FORS confirmed the presence of HgS due to the narrow and symmetric features centered at 590 nm in the first derivative spectra (Figure 5b) and a sharp s-shaped curve in the reflectance spectra indicative of a semi-conductor pigment [38]. In addition, Raman spectroscopic analysis of a dislodged red fragment in folio 50 r (Figure 5d) found in the gutter of the book was successful in firmly identifying cinnabar/vermilion as the red pigment ($254, 282, 343\text{ cm}^{-1}$). The minor peaks in the spectra ($136, 154, 202, 291, 311, 353$, and 382 cm^{-1}) showed an excellent match with natural orpiment (As_2S_3) [39]. Since other common arsenic sulfide pigments can be clearly distinguished by Raman spectroscopy, realgar and its alteration product, pararealgar, were ruled out. The intentional mixture of vermilion and orpiment is somewhat unusual and accounts for the yellow-orange appearance of these red decorations.

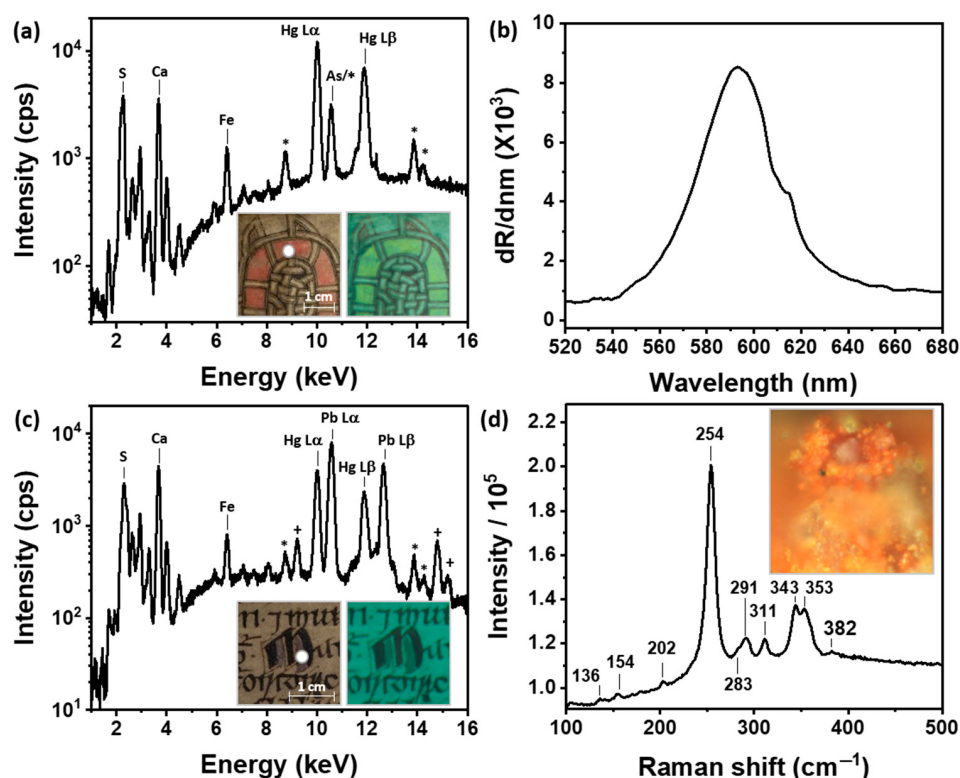


Figure 5. (a) XRF spectra of the red pigment cinnabar or vermilion. * represents other peaks for Hg. Insets show visible (left) and IRFC image (right) of the decorated initial letter in folio 48 r (quire 10). White dot in the visible image indicates where XRF analysis was performed; (b) FORS spectra confirming vermilion, folio 48 r; (c) XRF spectra of the red mixture of cinnabar/vermilion with Pb-based pigment/s. + indicates other peaks for Pb. Insets show visible (left) and IRFC image (right) of the decorated initial letter in folio 9 r. White dot in the visible image represents where XRF analysis was performed; (d) Raman spectrum, recorded using a 785 nm laser, confirms that cinnabar/vermilion and orpiment were used in mixture. Folio 50 r.

In contrast to what was found for the orange applications, the darker shades of red in quires 2, 5, 12, 18, 19, and 20 appeared as dark green in the corresponding IRFC image (see insets of Figure 5c), supporting the hypothesis that a different pigment mixture was used for these areas [40]. A representative XRF spectrum is shown in Figure 5c, performed on the rubricated letter M in folio 9 r. The spectrum was characterized by intense peaks for Hg and Pb, suggesting that for achieving these hues, cinnabar/vermillion was mixed with Pb-based pigment(s), more likely lead white [$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$] or minium (red lead; Pb_3O_4), which are known to degrade toward a gray color.

The elemental composition of the different red applications was plotted in a histogram where the relative (to Fe) concentrations of Pb, Hg, and As were plotted against the folios in the codicological order as it is today (Figure 6). This allowed two pigment mixtures to be distinguished: a mixture of cinnabar/vermillion with orpiment (discussed above), which was used in quires 1, 2, 9, 10, 11, 12, 13, 15, and 16; and a mixture of cinnabar/vermillion with Pb-based pigment(s) in various ratios, used in quires 2, 5, 12, 18, 19, and 20. This clearly showed a correlation between the use of specific pigments and the structure of the Book Uí Mhaine by quire and scribal hand, in line with the fact that the quires composing the volume were meant to be stand-alone productions.

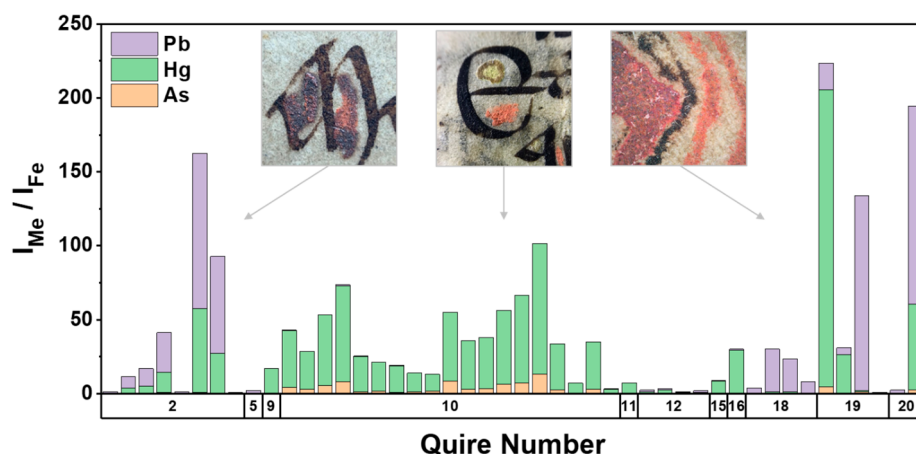


Figure 6. Histogram plotting the content of Pb, Hg, and As, ascribable to the presence of red cinnabar/vermillion, lead-based pigment(s), and orpiment (elements normalized to Fe). Insets: representative photographs of pigment applications in different red shades and yellow colorations.

Yellow decorations were found consistently in every folio of quire 10, written by Faelán, scribe, poet, and confidant of Bishop Ó Ceallaigh, for whom he prepared the most decorated gathering of the manuscript. Yellow applications were also found scattered in a few folios in quires 11, 12, 13, 14, 15, 16, 20, and 22. Yellow pigments were never found in conjunction with lead-based pigments in the same quires, but rather only in combination with vermillion. A total of twenty-six XRF spectra were obtained from yellow pigments throughout the book, revealing their similarity to one another. Figure 7a shows a representative XRF spectrum of a yellow pigment taken on an initial letter in folio 48 r. The elemental composition was characterized by prominent As and S peaks, indicating the use of an arsenic sulfide pigment. Fe, Ca, K, and Hg, along with traces of Cu and Zn, were also observed and were attributed to contributions from the background parchment or interpreted as contamination from adjacent ink and pigment areas. FORS analysis of yellow-pigmented areas, in conjunction with XRF, confirmed the presence of orpiment due to a sharp peak at 480 nm in the first derivative spectra and a steep stair-step shape in the reflectance spectra indicative of semi-conductor pigments (see Figure 7b) [41]. Further analysis was carried out by MSI, which showed visible yellow areas shifting into ivory-white coloration in the IRFC images (Figure 7d), in line with the literature [13]. In some instances, the yellow application had become imperceptible to the naked eye. In such cases, XRF analysis played a crucial role in indicating the previous presence of orpiment in these

areas. Notable examples can be observed in the yellow decorative line surrounding the initial letter (Figure 7c) and the line surrounding the text in the *probatio pennae* (Figure 7f) of folio 48 r. These specific details were elementally characterized using XRF for confirming As presence and subsequently emphasized through PCA processing. By processing the stack of 15 MSI images, 15 PCA images were generated. The selection of the PCA image that best captured solely the yellow applications was made by carefully examining both the visible image (which revealed remnants of orpiment decorations) and the PCA images together. By considering both sources of information in tandem, the most accurate representation of the yellow application was selected. In Photoshop, the grayscale PCA image was transformed into a yellow-scale image. Then the image histogram representing the color values of the image pixels was adjusted to exclude irrelevant pixels from the representation, such as those related to the background and/or the image noise. The resulting image was then superimposed onto the visible image of the corresponding folio, allowing for the reconstruction of the original positioning of the faded orpiment decoration (see Figure 7e,g). By overlaying the enhanced image onto the visible image, the original placement of the faded orpiment decoration was effectively restored and visualized.

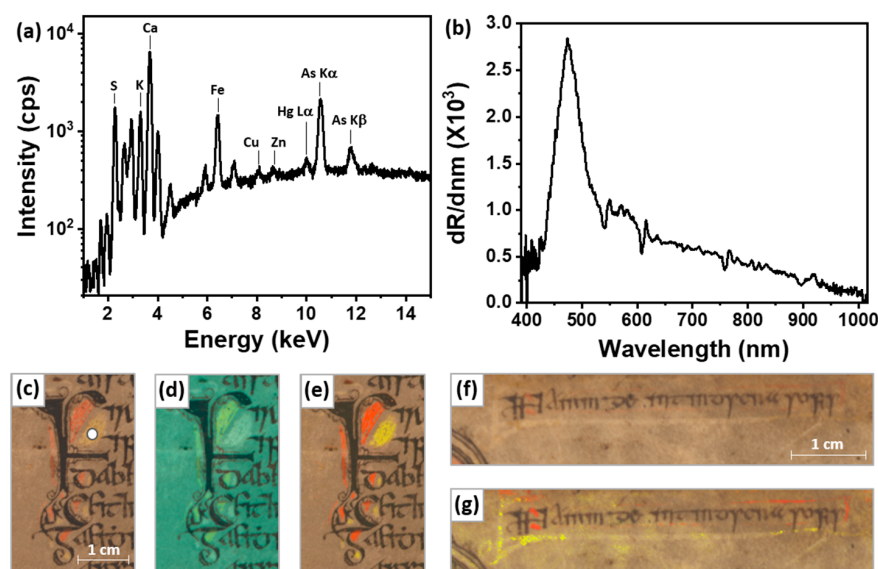


Figure 7. (a) XRF spectrum of a yellow pigment, folio 48 r; (b) Representative FORS spectrum of a yellow pigment, folio 54 v; (c–e) Visible image, IRFC, and PCA-based color reconstruction of the decoration of initial letter F (folio 48 r). White dot in visible image indicating the location where XRF spectrum was recorded; (f,g) Visible image and PCA-based color reconstruction of orpiment in *probatio pennae*, folio 48 r upper margin.

Given the somewhat unprecedented appearance of the mise-en-page of folio 111 r, and on the advice of codicologists and paleographers, further analyses were performed on this folio. In fact, the zoomorphic initial T (Figure 8a) stands alone in the decorative pattern of the book and presents a diverse palette of colors. For instance, it is the only decorated initial presenting green pigmentation. Its significance may be that it marks the beginning of the poem in praise of a famous Ó Ceallaigh chieftain, Uilliam Buidhe, who died in 1381.

The XRF spectrum of the warm red shade at the side of the animal head (Figure 8c, spot 16) showed intense peaks for Hg and Pb, suggesting that a mixture of cinnabar (bright red coloration) and Pb-based pigment(s) (dark coloration) was used. The XRF spectrum taken on the lighter red-pink hue of the figure (Figure 8d, spot 17) showed a similar ratio of Hg/Pb if compared to the darker red coloration. The overall lighter hue contribution could be associated with the presence of lead white, which was added to cinnabar to obtain the lighter red hue observed. Finally, the XRF of the purple/gray area (s18, Figure 8e) showed a prominent presence of Pb-based pigment(s), known to be prone to degradation towards brown and black colorations (galena, PbS) [42–44].

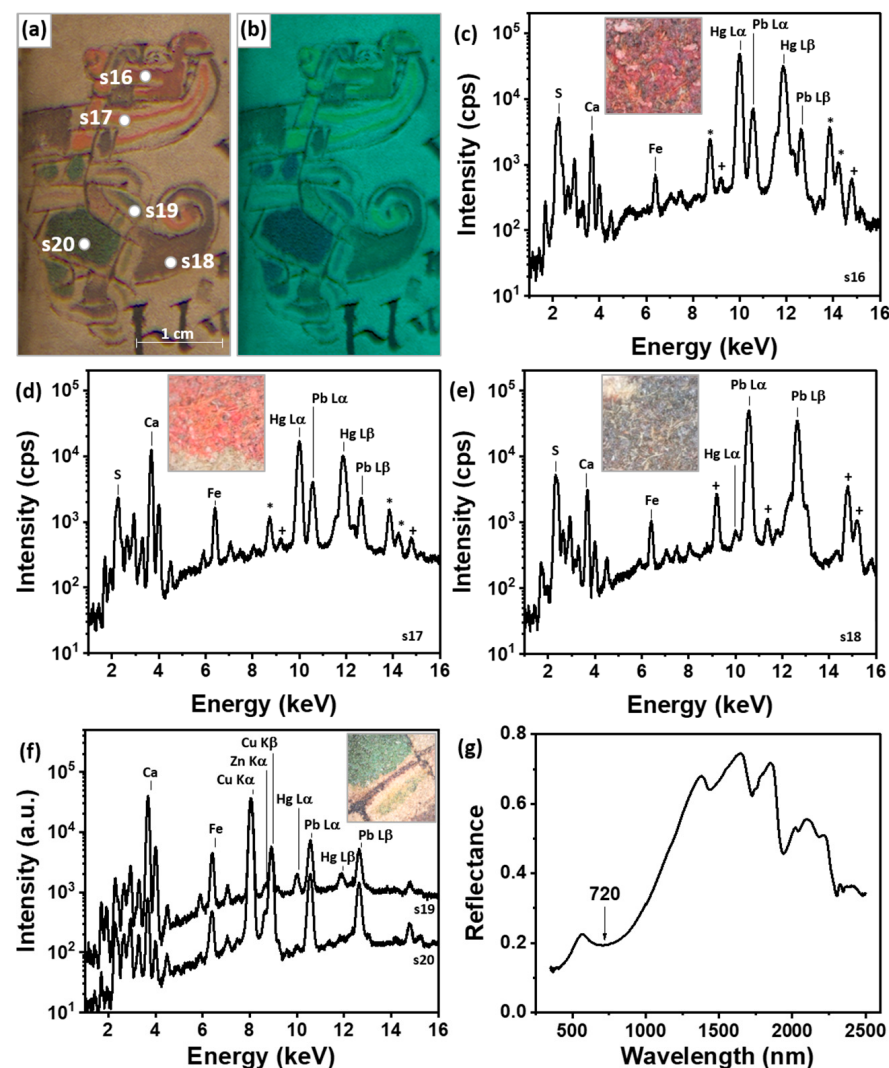


Figure 8. (a) Visible image and (b) IRFC of zoomorphic initial letter, folio 111r. White spots and numbering represent areas where XRF spectra were taken; (c–e) XRF spectra of spots 16, 17 and 18, respectively. Insets show microscopic optical images of the areas of analysis. * represents other peaks of Hg; + indicates other peaks for Pb; (f) XRF spectra of light green pigment (top spectrum, s19) and dark green pigment (bottom spectrum, s20); (g) FORS spectra of the dark green area (s20).

Six XRF spectra were performed on dark and light green on this folio. The elemental composition of these areas (see Figure 8f) highlighted that all greens were characterized by the presence of Cu and Pb. The lighter hues of green might have resulted from a lighter application or from a mixture with white pigment(s), either lead white or calcite, considering the more intense peak for Ca in these lighter areas when compared to darker green hues. However, as the analyzed light greens are thinner than the darker applications, it was difficult to exclude a substantial Ca contribution from the parchment. The presence of Fe was attributed to a contribution from the parchment background. Given that Hg was detected only in trace amounts, it was interpreted as contamination originating from the nearby vermilion applications, rather than being intentionally mixed with the green.

The green area appeared as blue in the IRFC image (Figure 8b), which aligns with the findings reported in the literature for most of the Cu-based greens. The FORS spectra (Figure 8g) exhibited a broad absorption centered at ~720 nm, indicating the likely presence of verdigris rather than other Cu-based pigments [45]. However, to fully confirm the presence of verdigris, further analysis would be necessary.

3.5. Pigment Degradation

Various causes of pigment degradation were identified and are highlighted in Figure 9.

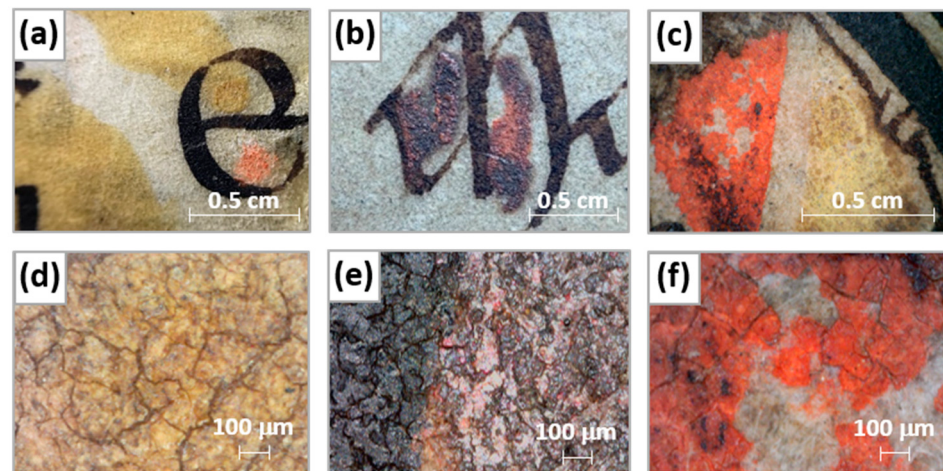


Figure 9. Optical microscopy images of pigment details across the book showing details of: (a,d) pigment migration and smudging; (b,e) pigment color change; (c,f) pigment detachment.

Degradation by spreading/smudges due to the water solubility of pigments exposed to humidity was observed (see Figure 9a and close-up Figure 9d), particularly accentuated in applications made of orpiment. Color degradation by color alteration was commonly observed. This process is shown in Figure 9b,e for the specific case of a red rubrication changing color into dark gray, a phenomenon likely associated with the chemical transformation of Pb-based pigments into galena (PbS). The other source of degradation observed was a color loss by detachment (see Figure 9c and close-up Figure 9f), likely associated with the degradation of the binding medium. This resulted in heavy cracking and flaking of the folios. This induced both poor adhesion to the support and loss of cohesion between particles, therefore resulting in detachment from the parchment support.

4. Conclusions

A multi-analytical approach was used for the first time to analyze the materiality of an Irish Gaelic manuscript from the medieval vernacular period. Protein analysis confirmed the use of skin from young calves in the production of the parchment. Additionally, a combination of XRF and MSI allowed the identification of writing inks, decorative practices for capital letters, and techniques for ruling the parchment prior to writing. The analysis of pigments using XRF, FORS and MSI allowed the identification of vermillion and Hg/Pb mixtures used for reds and the use of orpiment for yellows. Notably, a copper-based green was found solely in the decoration of a single folio. Several questions still remain unanswered, particularly regarding the origin of the Pb-based material used for ruling the folios and the cause behind the ink's persistent dark coloration in infrared images at 940 nm. Additionally, the cause of the degradation of the red pigment mixture (Pb/Hg), which displayed a shift in color towards a metallic purple/gray hue, is unknown. To address these queries, the use of sampling-based techniques would be beneficial. These techniques could provide valuable insights and help shed light on the uncertainties mentioned earlier. Moreover, obtaining samples would open up possibilities for understanding the organic components present in inks and pigments. Although this investigation focuses specifically on the Book of Uí Mhaine, the knowledge acquired from this research is anticipated to support future studies in the field by enhancing our understanding of the production of medieval manuscripts within the Gaelic tradition and beyond.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/heritage6070284/s1>, Table S1: Classification of the Book of Uí Mhaine by scribe, quire and folios according to William O’Sullivan; Figures S1 and S2: High-res photographs of stain patterns and ink transfer; Figure S3: Ink transfer from f. 2 v to f. 3 r; Figure S4: Ink transfer from f. 3 v to f. 4 r; Figure S5: Graphic ruling in folio 20 v.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding author, DI, upon reasonable request.

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