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HERALDIC ART ON PAPER: TECHNICAL ANALYSIS OF THE MATERIALS AND PAINTING TECHNIQUES IN 17TH-CENTURY ILLUMINATED MANUSCRIPTS FROM IRELAND

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ABSTRACT The early modern period in Ireland was marked by war and political turbulence, which disrupted all spheres of life, including artistic production. Consequently, few examples of Irish visual art survive from this period, leaving a gap in our understanding of the materials and techniques used by Irish artists. This study is the first investigation of colorants present in three 17th-century illuminated heraldic manuscripts on paper, which are part of the National Library of Ireland's collections. Technical analysis was conducted using non-invasive analytical techniques (VIS-SWIR FORS, pXRF, microscopy). The choice of colorants varies according to each manuscript and corresponds to the work by different heralds over a 50-year period. More than 12 different colorants were identified in various combinations, including azurite/blue verditer, indigo/woad, smalt, cinnabar/vermilion, red lead, insect-based red lake, arsenic sulphide yellow, yellow lake, shell gold, copper-based green, vergaut, carbon black and iron gall ink. We detected evidence of altered azurite and degraded vermilion, which negatively impacted the visual integrity of the images. The production, in Ireland, of these heraldic manuscripts is in line with wider European artistic traditions; the materials identified correspond with artists' treatises and trade records, and with the results of other analysed European illuminated manuscripts of the period.

Introduction to heraldic art and the NLI heraldic manuscript collection

The large collection of heraldic manuscripts of the National Library of Ireland (NLI) includes 38 volumes with unique illustrations of armorial bearings.[1] The manuscripts document key players and pivotal events in the history of the Irish nation and its intricate relationship with its neighbouring nations of England, France and Spain in the 16th and 17th centuries. The early modern period saw intense political conflict in Ireland: the Nine Years War, the Jacobite/Williamite War and the Confederate/Cromwellian war caused widespread destruction, the latter resulting in a 20–40% loss in the population.[2] Heraldic manuscripts were safeguarded and preserved because they represented a crucial aspect of the new English ruling powers' assertion of control and ownership over Ireland. The survival of the NLI's heraldic manuscripts also stands as a testament to historical serendipity. The collection never found its way into the Public Records Office which had succumbed to fire during the Civil War in 1922, thus these heraldic manuscripts are irreplaceable evidence of Ireland's heritage.[3]

Heraldic art deals with the design and depiction of armorial bearings: a coat of arms with accompanying devices (helmet, crest, supporters, motto), which served as regular, hereditary designs to signify an individual or group.

Figure 1 Four of the nine folios analysed (in normal light). A: GO MS 44 (1606) fol. 1r. B: GO MS 46 (*c.*1649–56) title page. C: GO MS 64 (1588–1617) fol. 4v. D: GO MS 64 fol. 5v (photos: National Library of Ireland).

Although heraldic images first appeared on shields across many European countries, their earliest expression on documentary heritage can be found in seals produced in England from the end of the 12th century[4] and in illuminated manuscripts, such as the grants of arms produced by the Imperial Chancery in the 13th century.[5]

The Office of the Ulster King of Arms was established in Dublin in 1552 to control the use of armorial bearings in Ireland and by extension the tenure of landed estates, by a colonial political authority, the English Crown. It was modelled on the College of Arms in London[6] and there was direct contact between the two offices.[7] The heralds were based in Dublin Castle, the administrative centre of the English Crown in the Pale, the Protestant-dominated eastern region of Ireland. They were a visible and prestigious part of the English Crown in Dublin, responsible for 'advising on state ceremony, protocol and precedence and participating in state processions'.[8] As well as designing, certifying and recording official documents on heraldic descent, a herald also made visual records of ceremonies where arms were officially and ostentatiously displayed, such as coronations and royal and noble marriages and funerals.[9]

In heraldry, emblazoning refers to the meticulous process of designing and painting a heraldic device. The art of emblazoning follows strict rules and language to visually communicate the blazon, the verbal description of arms in heraldic language. To paint armorial bearings, heralds used a limited prescribed colour scheme known as a tincture: gules or red; sable or black; azure or blue; vert or green; purpure or purple. Metals (silver and gold) were frequently used or were represented by white and yellow paint.[10] The herald was therefore also an artist and in this paper is identified as artist-herald.

The establishment of the Guild of Saint Luke in Dublin city in 1670 indicates a rise in artistic production following cessation of the conflicts. However, only a few artefacts survive from this century to offer artistic context. One rare group of surviving contemporary works from the early modern period are manuscript maps created by English cartographers, commissioned by the English Crown to survey and document the island of Ireland.[11] The surviving examples of 17th-century portraiture in easel painting were either painted abroad and brought back to Ireland or commissioned from travelling foreign artists.[12] Some polychrome funerary monuments, often depicting arms created for newly settled English families, still exist in homestead churches around Ireland.[13]

Heraldic manuscripts, featuring a rich palette applied according to prescribed rules, provide a unique perspective for studying the use of colorants in Ireland. This article aims to investigate and document, for the first time, the use of colorants in 17th-century Irish heraldic manuscripts. By characterising the materials and painting techniques used by artist-heralds in three rare manuscripts, the study provides new insights into the exchange of techniques and the history of trade in artists' materials, situating these practices within the broader context of European artistic traditions.

Materials and methodology: selection of manuscripts and non-invasive analytical techniques

As a case study, three manuscripts from the NLI heraldic manuscript collection were selected for technical analysis on the basis that these were the earliest manuscripts that were clearly dated, signed and known to be produced in Dublin. In addition, they present deterioration phenomena which require investigation to make informed conservation decisions. The first manuscript investigated is titled 'British Families in Ireland' (GO MS 44) signed and dated in 1606 by Daniel Molyneux (1597–1632), Ulster King of Arms (Figure 1A); the second titled 'Funeral Entries' (GO MS 64) with a similar date (1588–1617) is unsigned (Figure 1B); the third titled 'British Families Cromwell's Officers' (GO MS 46) is signed and dated *c.*1649–56 by Albon Levert, Athlone Officer of Armes (active 1608–d.1661) (Figure 1C and 1D). Each manuscript contains folios with illustrations drawn with pen and ink and painted in vivid opaque watercolour on paper. Some graphite underdrawing is perceptible, and there are areas of graphite and blind ruling on some folios. The paper is linen or cotton handmade paper, and within each manuscript partial watermarks of different common European motifs are found.[14] The manuscripts (average dimensions 300 × 215 mm) were bound into reverse calf leather bindings in the 19th century. As well as graphic art, the manuscripts were working documents of the heralds and there are extensive passages of text written in ink, often with graphite notations.

Technical analysis of the manuscripts began with the naked eye, both under visible (direct and raking) and ultraviolet (UV) light, followed by microscopic examination under magnification (7.5–200×).[15] This facilitated investigation of morphological details of the image layer, painting techniques, modelling of draperies, fleshtones, outlines, pigment mixtures, layering and glazes, particle size and shape, fluorescence phenomena typical of organic materials, and evidence of degradation. Precise material identification was conducted using more thorough instrumental analysis.

Point analysis of the different materials in the illuminations with non-invasive spectroscopic techniques followed, namely: ultraviolet-visible-short wave infrared fibre optic reflectance spectroscopy (UV-VIS-SWIR FORS) in the range 230–2500 nm,[16] and portable X-ray fluorescence (pXRF) spectroscopy.[17] The spots were carefully selected for analysis to capture the full range of colorants present and to document the degradation phenomena observed in the media layer across nine folios.

Results and discussion

Pigments identified and the degradation phenomena

The results are presented categorised by colour and manuscript in chronological order: GO MS 44 (1606), GO MS 64 (1588–1617) and GO MS 46 (*c.*1649–56), noting similarities

Table 1 Summary of the NLI heraldic manuscripts analysed and materials identified (* indicates those pigments that show noticeable degradation).

Heraldic manuscripts investigated from the National Library of Ireland			
Reference	GO MS 44	GO MS 64	GO MS 46
Title	*British Families in Ireland*	*Funeral Entries*	*British Families Cromwell's Officers*
Date	1606	1588–1617	*c.*1649–56
Artist-herald	Daniel Molyneux	Anonymous	Albon Levert
Folios analysed	1r, 3r, 21r, 46r	4v, 5v	Title page, frontispiece, 1r
Blue	Copper carbonate (azurite or blue bice/verditer);*[1] indigo/woad	Copper carbonate (azurite or blue bice/verditer)*[1]	Smalt; indigo/woad
Red	Cinnabar/vermilion + red lead; mixture of cinnabar/vermilion + lead-based pigment + chalk or gypsum;*[2] insect-based red dye as glaze	Cinnabar/vermilion + red lead	Cinnabar/vermilion + red lead; insect-based red dye as glaze
Pink	Red lake: insect-based dye on gypsum	N/A	Red lake: insect-based dye on gypsum
Fleshtones	Mixture of cinnabar/vermilion + lead-based pigment + chalk or gypsum;*[2] red lead + cinnabar/vermilion	N/A	Red lead + cinnabar/vermilion
Yellow	Orpiment/arsenic sulphide glass; shell gold	Orpiment/arsenic sulphide glass; metallic yellow powder (not gold)	Yellow lake: organic yellow dye on gypsum
Green	Malachite or verdigris + vermilion/cinnabar + tr. orpiment/arsenic sulphide glass; azurite/blue bice mixture	Vergaut (indigo/woad + orpiment/arsenic sulphide glass)	Azurite/blue bice mixture
White	Gypsum	Paper background	N/A
Black	Carbon-based	Carbon-based	N/A
Ink	Iron gall	Iron gall	Iron gall
***Degradation products**	[1] Degradation of azurite: green copper chlorides [2] Darkening of cinnabar/vermilion or the lead-based pigment in the mixture	[1] Degradation of azurite: green copper chlorides	N/A

and differences. A summary table with the details about each manuscript analysed and the materials identified is presented in Table 1.

Blues

In GO MS 44, a hydrated copper carbonate, either the mineral azurite or its synthetic counterpart blue verditer, was identified in the brighter blue areas in the coat of arms and draperies of fol. 1r, by its characteristic absorption bands in the FORS spectrum (*c.*638, 1498, 2211, 2287, 2354 nm) (Figure 2) and the detection of copper by pXRF. Indigo or woad, a deep blue dye obtained from plants from the *Indigofera* and *Isatis* species respectively, was used by the artist-herald in the same illustration for the duller blue-grey tones, for instance in the armour, as shown by its asymmetric absorption band at c.658 nm in FORS (Figure 2).

Azurite/blue verditer was also identified in the blue areas of fol. 4r GO MS 64 by FORS (absorption bands at *c.*632, 1492, 2285, 2352 nm) (Figure 2) and pXRF (detection of copper and calcium). In this case, a green alteration was observed in some areas (Figure 3A), and pXRF analysis showed that it contained chlorine and sulphur. This is a typical indicator of azurite degradation, as humidity and chloride ions – originating from marine aerosols, pollution or impurities in the pigment or the binder – lead to the formation of green chlorides, such as nantokite, paratacamite/atacamite or botallackite.[18]

In 1649, the artist-herald who painted the title page of GO MS 46 selected smalt, ground potassium glass, as a blue. This colorant is recognised by three characteristic absorption bands in the FORS spectrum (542, 591, 643 nm) (Figure 2). In the 17th century, the northern Netherlands

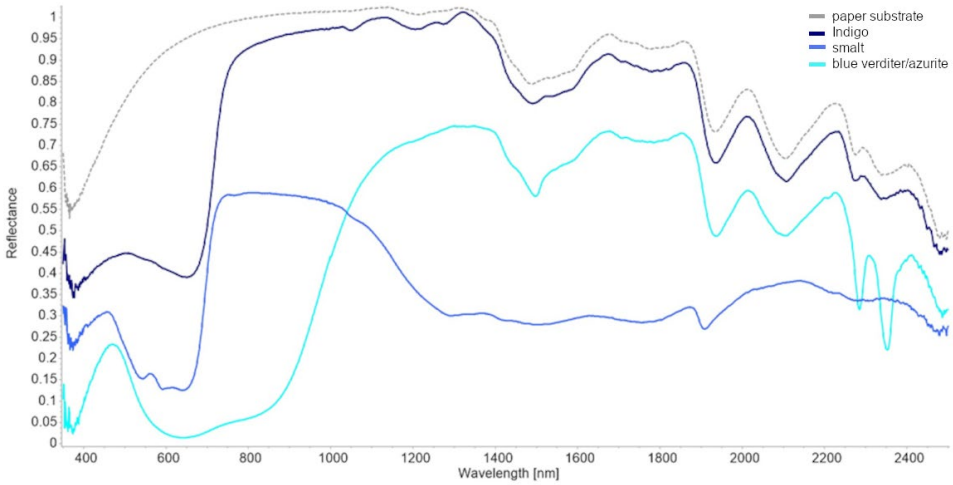

Figure 2 FORS spectra of blue pigments found across the three manuscripts: light blue: azurite; medium blue: smalt; dark blue: indigo; grey: paper substrate.

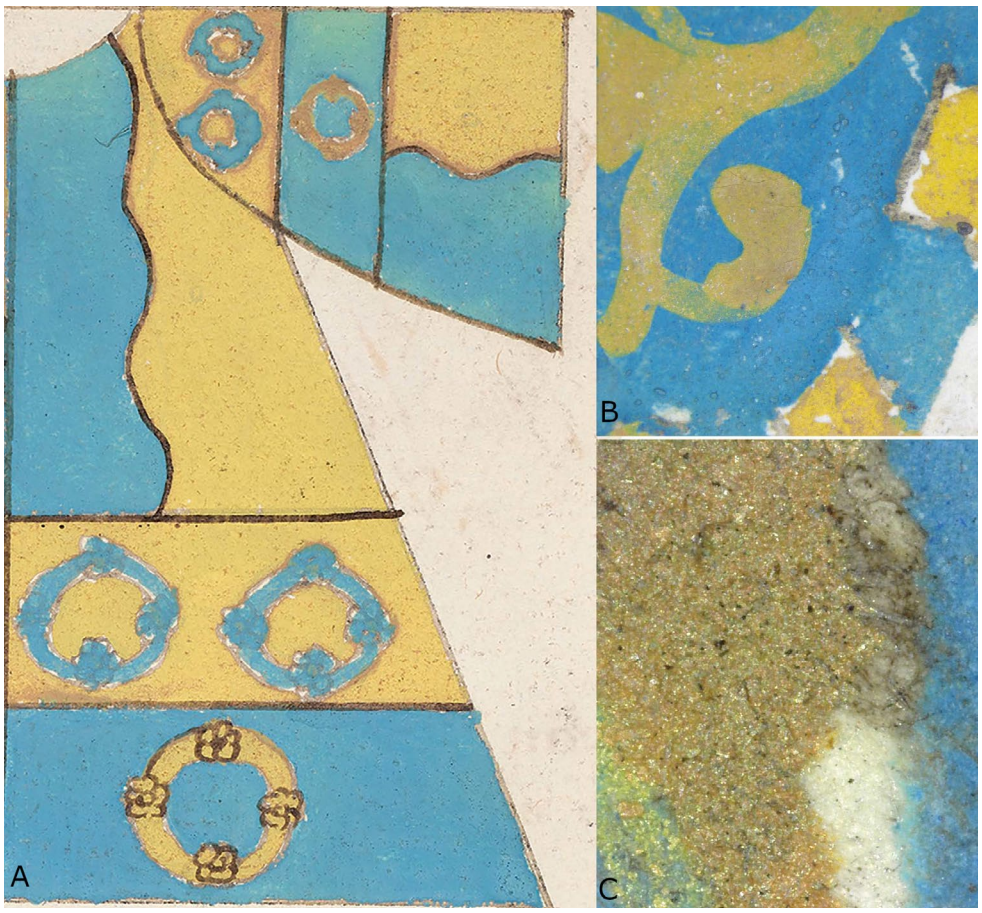

Figure 3 GO MS 64 (1588–1617): details of fol. 4r. A: alteration of blue colorant, identified as azurite; B: yellow metallic paint was applied on top of some blue areas (7.5× normal light photomicrograph); C: detail of metallic colorant (200× normal light photomicrograph).

specialised in the manufacture of smalt. Concurrently, due to a scarcity of azurite, the use of smalt as an artists' pigment became widespread across Europe.[19] In GO MS 46, smalt appears coarsely ground when observed under magnification, and the blue paint shows poor adhesion to the paper (Figure 4B). On the same folio, indigo/woad (FORS absorption at *c.*557 nm) was used for the grey-blue tone of the armour of the figures (Figure 4A).

Reds, fleshtones and pinks

Red areas were painted with mercury sulphide (either natural cinnabar or synthetic vermilion, which are chemically identical: HgS) in the three manuscripts analysed, as the pigment's characteristic transition edge at 600 nm was observed in the FORS spectra (Figure 5) and both mercury and sulphur were detected by pXRF. Lead was also identified by pXRF, suggesting that mercury sulphide was mixed

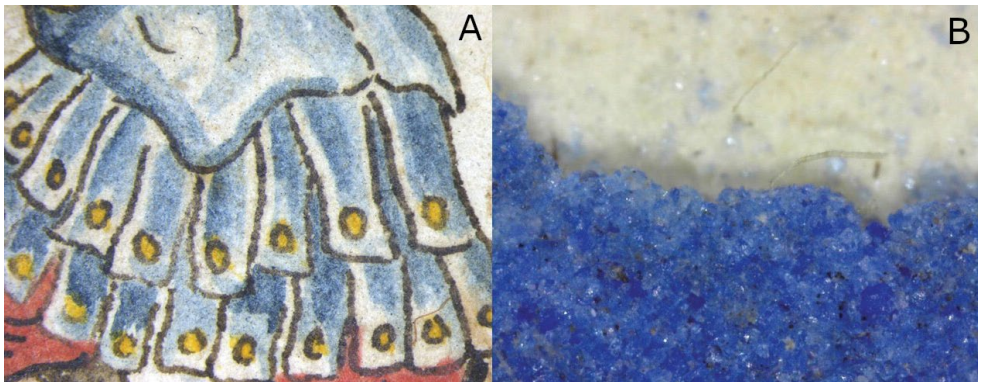

Figure 4 GO MS 46 (*c*.1649–56) title page. A: indigo was applied in graduated light washes on the armour of the figures (7.5× normal light photomicrograph); B: detail of smalt showing coarse grinding of the glass and detachment from the paper (200× normal light photomicrograph).

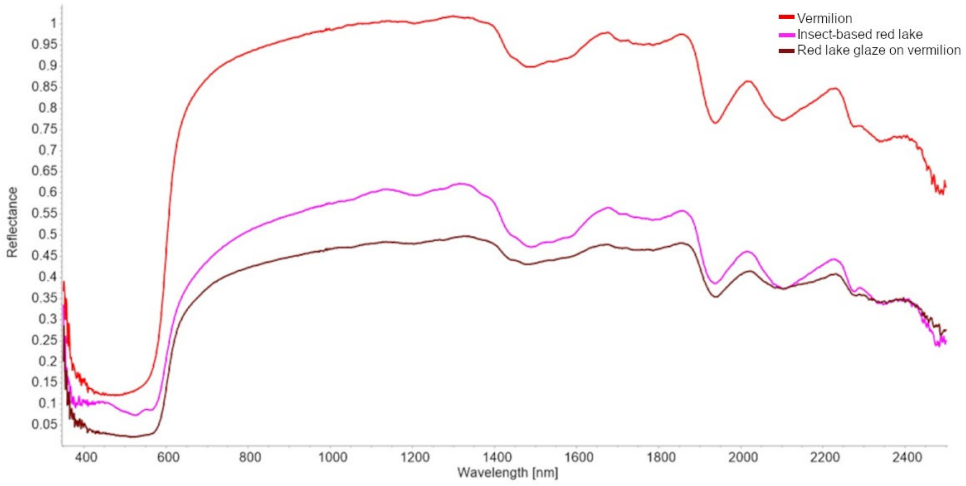

Figure 5 FORS spectra of red and pink areas found across the three manuscripts: red: vermilion; pink: insect-based red lake; dark red: red lake glaze on top of vermilion.

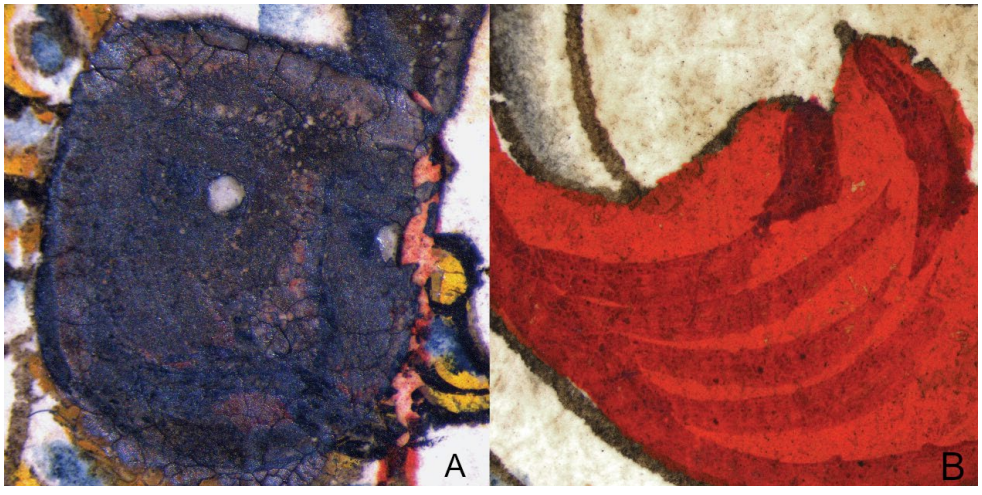

Figure 6 GO MS 44 (1606), fol. 1r. A: darkening of fleshtones on the face (5× normal light photomicrograph); B: red lake glaze applied over the red base layer to create a tri-dimensional effect on the feathers (7.5× normal light photomicrograph).

with a lead-based pigment, such as red lead (lead oxide), either deliberately (to obtain orange hues) or inadvertently (as it was a cheap pigment commonly used to adulterate vermilion).

In GO MS 44, the fleshtones of the figures in fol. 1r and some of the red foliage of fol. 46r have undergone extensive darkening to a silvery-grey colour (Figure 6A). In both cases, pXRF analysis shows an elemental composition of Hg, S, Pb and Ca, suggesting a likely mixture of mercury sulphide (HgS), a lead-based pigment such as lead white ($2PbCO_3 \cdot Pb(OH)_2$) or red lead (Pb_3O_4), and either chalk ($CaCO_3$) or gypsum ($CaSO_4 \cdot 2H_2O$), which could have been used as a white pigment or as the substrate of a red dye. The FORS spectra were uninformative in this instance because

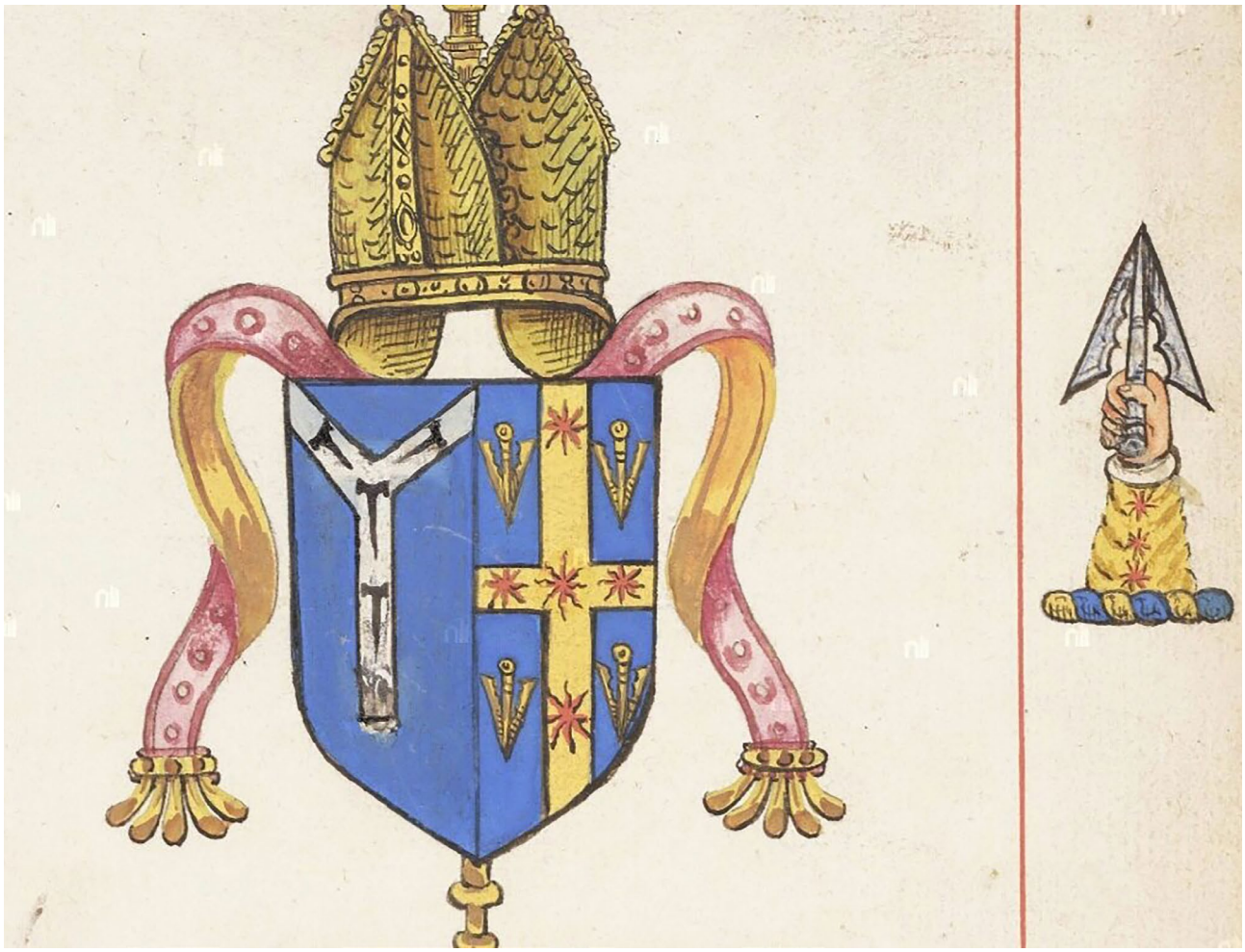

Figure 7 GO MS 44 (1606): detail of fol. 3 (in normal light). The fleshtones of the hand on the right-hand side have not discoloured as seen in **Figure 6A**, indicating a different mixture of colorants with a light orange tone. The white pigment applied to the shield was identified as gypsum.

the media layer in these areas had undergone discoloration and darkening, preventing the display of any characteristic reflectance features. Therefore, the degradation product could not be identified with the analytical techniques available. However, based on the published literature about this pigment's degradation and the colour of the altered areas, it is likely that the red mercury sulphide underwent degradation when exposed to light and silvery-grey elemental mercury was formed.[20] In contrast, the fleshtones of the hand of fol. 3r, GO MS 44 (Figure 7) and in GO MS 46 have not degraded. A light orange tone is visible here, identified as a mixture of red lead and cinnabar/vermilion, based on the FORS results (transition edge at *c.*576 nm).

An insect-based red dye, such as cochineal, was used for the pink tones present in fol. 3r, GO MS 44 (Figure 7) and GO MS 46; the typical absorption bands at *c.*492, 524 and 565 nm were observed in the FORS spectra (Figure 5). Calcium sulphate, like gypsum, seems to have been used as the substrate to precipitate the dye and make a lake pigment, based on the pXRF results (Ca, S) and three characteristic absorption bands in the FORS spectrum (*c.*1440–1590 nm). An insect-based red dye was also applied as a glaze on top of the red areas in these manuscripts to model feathers and fabrics, rendering them more three-dimensional (Figure 6B). In the illustrations of GO MS 64, there are no fleshtones present.

Yellows and browns

In GO MS 44 fol. 1r, arsenic and sulphur were identified by pXRF in the yellow areas. Raman analysis would be necessary to identify with certainty the type of arsenic sulphide used here, but we suggest the most likely pigments are either the deep orange-yellow mineral orpiment (As_2S_3), widely used in manuscript illumination in Europe, or its synthetic counterpart, an arsenic sulphide glass, also identified on 17th-century maps made in Ireland by Tudor mapmaker Richard Bartlett.[21] Brushstrokes of shell gold were applied on top of the yellow paint in some areas of fol. 1r of GO MS 44 to create highlights (Figure 8A). In GO MS 46, an organic yellow dye, such as weld, was found, in contrast with the orpiment present in the other two manuscripts (Figure 8B). The dye was likely precipitated onto a gypsum substrate to make the lake pigment, as S and Ca were detected by pXRF, and the absorption bands of gypsum were observed in the FORS spectrum (*c.*1440–1590 nm). On fol. 5v, GO MS 64 an arsenic sulphide yellow (orpiment or synthetic glass) was also used, as As and S were detected by pXRF (Figure 8C).

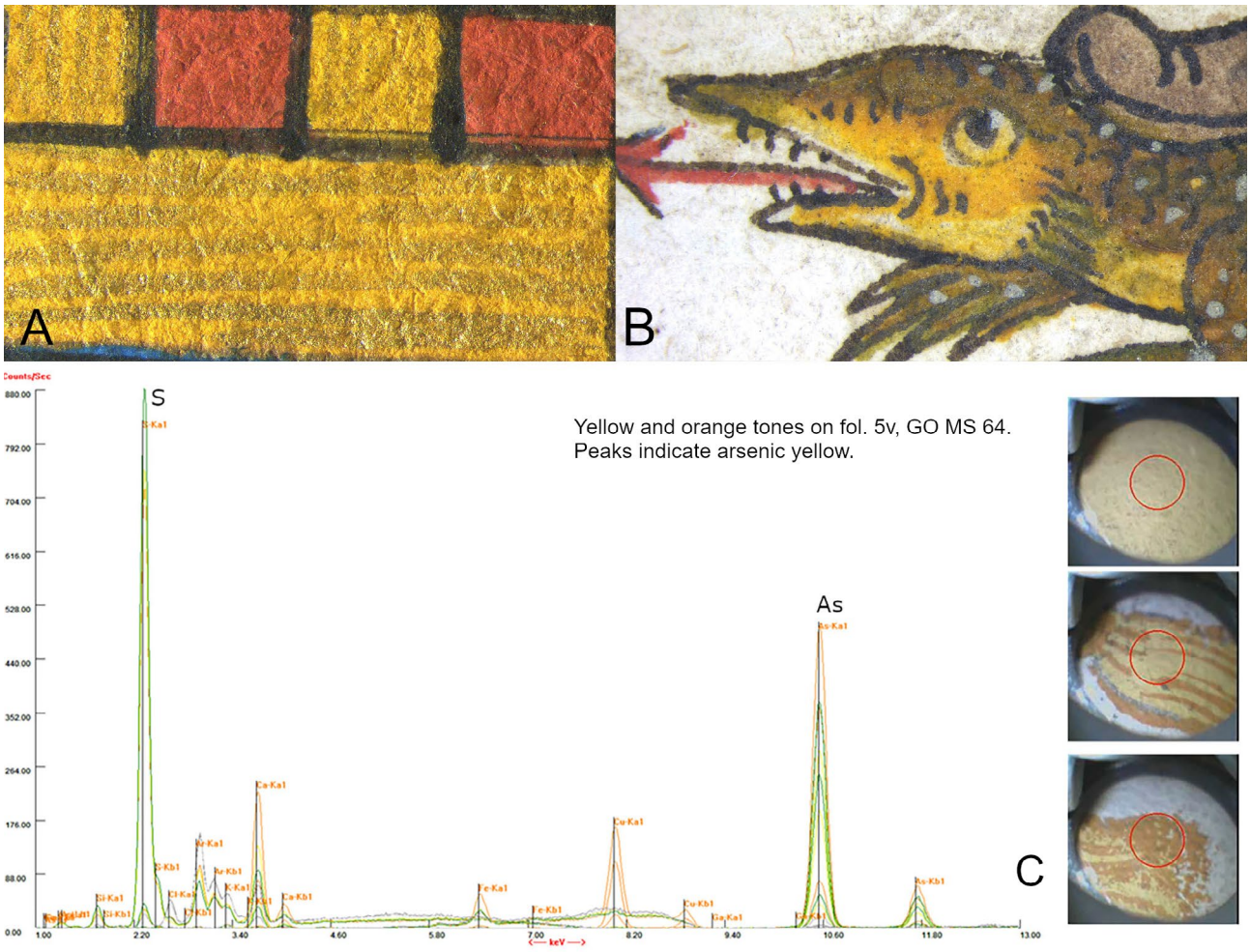

Figure 8 A. GO MS 44 (1606), fol. 1r: shell gold over orpiment/arsenic sulphide glass (7.5× normal light photomicrograph). B. GO MS 46 (*c.*1649–56), title page: organic yellow dye (200× normal light photomicrograph). C. GO MS 64 (1588–1617), fol. 5v: XRF spectra of yellow and orange areas showing the presence of arsenic and sulphur.

Characterisation of browns in the ground of GO MS 44 fol. 1r and the boots of the figures depicted in the title page of GO MS 46 (Figure 8A) has been challenging and inconclusive. Browns may be composed of complex mixtures containing ochre pigments, as suggested by the shape of the FORS spectra.

A yellow metallic paint was applied on top of some blue areas in fol. 4v of GO MS 64 (Figure 3B and 3C), but gold (Au), tin (Sn) or zinc (Zn) were not found by pXRF. This indicates that gold, mosaic gold (SnS_2), bronze powder (Cu and Sn alloy) or brass powder (Cu and Zn alloy) were not used as colorants. Copper (Cu), arsenic (As) and sulphur (S) were detected in the metallic pigment, but the presence of these elements is most likely related to the azurite/blue verditer and arsenic sulphide yellow in the paint layers underneath. The components of the yellow metallic paint therefore remain unidentified.

Greens

In GO MS 44 two shades of green were observed and analysed. The first shade is a bluish green (Figure 9A) in the arms of fol. 21r of GO MS 44. It is a mixture of blue azurite/blue verditer (identified by the absorption bands in FORS *c.*632, 842, 1498, 2284 and 2351 nm), and an unidentified yellow pigment. On the title page of GO MS 46, a similar mixture is likely present in the green shade (Figure 8B).

The second shade is a pale green in the grass of fol. 1r (Figure 9B). Under magnification a glassy cracked surface is visible. The green absorbs UV light strongly, indicating it is inorganic. There is visible strike-through on the back of the green passages, common to copper-containing colorants. According to the pXRF results, it is a mixture of a copper-based pigment (such as malachite or verdigris), vermilion and traces of arsenic sulphide (orpiment). Indigo/woad may also be present, as indicated by an absorption band at *c.*660 nm in the FORS spectrum of this area.

In GO MS 64, the olive-green tone of the birds on fol. 5v (Figure 1D) is made with vergaut: a mixture of blue indigo (identified by the absorption at 660 nm in FORS) and yellow orpiment (as arsenic and sulphur were detected by pXRF).

White and black

Across the three manuscripts analysed, as is common in heraldic art, there is little white pigment used to achieve

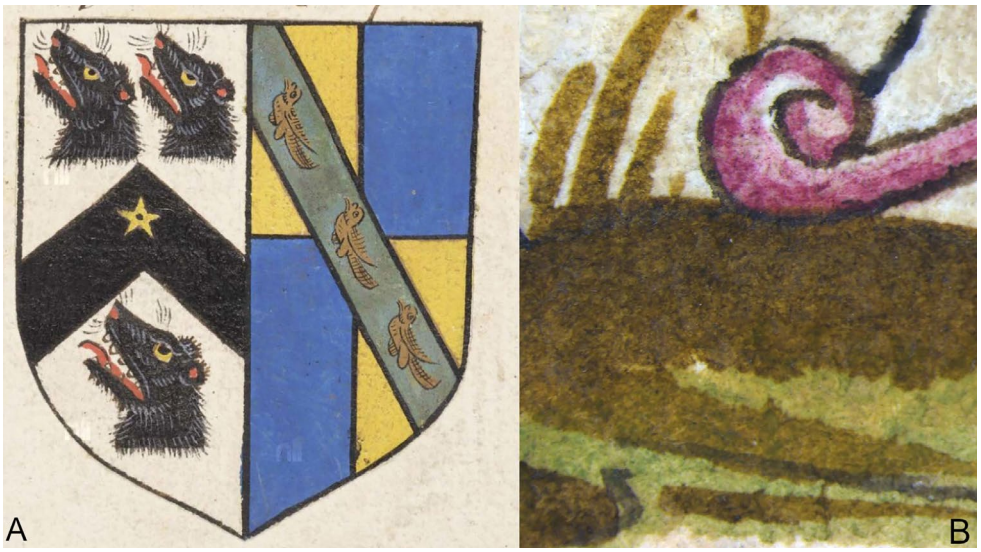

Figure 9 GO MS 44 (1606): two greens were found. A: Green on the arms of fol. 21r is a mixture of blue azurite/blue verditer and unidentified yellow pigment. B: Green on fol. 1r contains a copper-based pigment, vermilion and traces of orpiment (7.5× normal light photomicrograph).

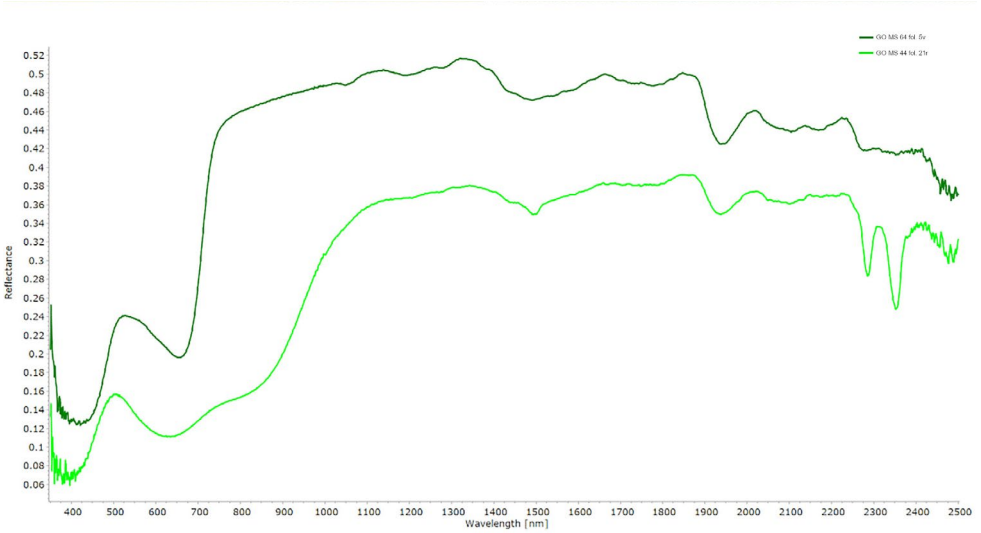

Figure 10 FORS spectra of green areas found across the three manuscripts. The dark green spectrum indicates vergaut is present on fol. 5v of GO MS 64 (1588–1617) and the light green spectrum indicates an azurite mixture on fol. 21r of GO MS 44 (1606).

tonal variation. Instead, the paper substrate is either left bare or visible under a colour wash (Figure 1). On fol. 3r of GO MS 44, the white band on the shield (Figure 7) was analysed with FORS; the spectra shows the absorption bands of gypsum (1448, 1500, 1530 nm and likely 2082 and 2133 nm), which was also found as the substrate of most lake pigments used in these manuscripts. Black pigments are probably carbon-based, as no inorganic elements were detected by pXRF.

Inks

The brown ink used for the text in the three manuscripts is likely iron gall ink, based on the high amount of iron detected by pXRF and the ink of the red text and ruling is vermilion/cinnabar, as both mercury and sulphide were detected.

Interpretation and contextualisation of the materials identified

This section explores the analytical results of the painting materials used in the three heraldic manuscripts analysed at NLI. By comparing these materials, the study aims to identify similarities and differences that may be attributed to chronological shifts or the personal preferences of distinct artist-heralds. To provide a comprehensive understanding, the results are contextualised with research from documentary sources, including early modern colouring treatises, records of pigment importation into Ireland, and archaeological evidence of trade in Dublin. Finally, the analysed materials were compared with the painting materials identified through analysis of other 16th- and 17th-century art on paper (illustrated manuscripts, maps), including the few

cases produced in Ireland in the period and examples from other countries in western Europe. For clarity and brevity, these comparisons are summarised in Table 2.

The illustrations in the three heraldic manuscripts employ the key heraldic tinctures: blue, red, yellow and green. Some pigments are used across the three examples such as cinnabar/vermilion for red hues. However, the manuscripts also exhibit significant variations in the painting materials and techniques used. In general, the artist-herald responsible for GO MS 64 uses unmixed colours and a simpler palette. Molyneux in GO MS 44 and Levert in GO MS 46 employ a broader selection of colorants and utilise more complex techniques, such as mixing and glazing, to achieve subtle variations in hue. This is evidenced by their use of different shades of blues and greens, as well as pink tones and deeper reds created by glazing vermilion with an organic dye. There is also a difference in the use of yellow pigments: GO MS 46 contains an organic yellow dye, likely weld, whereas orpiment is found in the other two manuscripts. The choice of greens seems to be particular to each artist-herald: in GO MS 44, a copper-based green (malachite/verdigris) is used, while GO MS 64 is the only case where vergaut was found, and in GO MS 46 azurite mixtures are favoured. Levert, in GO MS 46, is the only artist-herald to use smalt for blues and an organic yellow such as weld. The earlier artist-heralds preferred copper-based blues (azurite/blue bice) and arsenic sulphide yellows (orpiment/AsS glass). To determine whether this was due to personal choice or a change in practice over time, more examples from the NLI heraldic manuscript collection could be analysed. Ideally this would help to establish chronological trends and markers for some artists, which may assist in the attribution of unsigned manuscripts.

Some pigments have undergone degradation, which has transformed the original colours and impacts how these unique images are now perceived. The fleshtones in GO MS 44, now a dark grey tone, would have initially appeared orange pink, as seen in other folios not affected by the degradation. Equally, the blues in GO MS 44 and GO MS 64 would have appeared less turquoise in hue before the formation of green copper chlorides. The exposure to light and chlorine ions, probably from marine aerosol since Dublin is a port city, may have played a role in the degradation processes observed in both manuscripts.

In the 17th century, the technique of painting with water-soluble pigments bound with a medium such as gum (now known as watercolour painting) was referred to as limning. Several treatises on limning describe the preparation of pigments and the methods to apply colour to paper or parchment, and include information on blazoning of arms. In his 1612 edition of *The Gentleman's Exercise*, Henry Peacham (1578–1644?) includes a section on painting armoury and assigns the art of limning a particular status by describing it as an activity fit for a gentleman.[22] Another writer was Edward Norgate (1581–1650), an experienced miniaturist, scrivener and a herald in the College of Arms in London. His widely copied treatise *Miniatura or the Art of Limning* (1627) focused on portrait painting on parchment.[23] Thirdly, John Guillim (1551–1621) was a junior officer of Arm (*Rouge Pursuivant*) at the College of Arms in London. Guillim's manuscript, written between 1582 and 1604, is described as 'a handbook of pertinent techniques for the heraldic artist'.[24] Heralds working in Dublin may have learned limning techniques indirectly from these contemporary treatises: they are important resources in contextualising and interpreting the results of the technical analysis of the NLI heraldic manuscripts.

All the colorants identified in this project are in line with the materials listed in these 17th- century colouring treatises. Peacham lists 29 colorants, including the use of shell gold.[25] He also notes the following 10 pigments, which were either not detected in this study or could not be confirmed with the techniques used: carbon blacks, saffron, massicot, sap green, orchil, litmus blue, rosette, earth colours, red ochre (sinoper toppes, sinoper lake). Norgate lists a similar group of 25 colorants commonly used in limning: ultramarine and asphaltum are noted but not found in this study. Norgate does not recommend the use of verdigris or orpiment in limning, as found in the NLI heraldic manuscripts, as he considered them only fit for colouring prints and maps.[26] Guillim also lists a similar group of 25 colorants, but red orpiment (realgar), dragon's blood, gold foil and silver foil were not found in this study.[27] The technique of glazing red areas with red lake to achieve a three-dimensional effect observed in GO MS 44 (Figure 7), was an established method that Guillim records and which is found in contemporary easel paintings.[28]

The analytical results were cross-referenced with records of colorant importation into Ireland. There is little evidence that colorants were produced in Ireland[29] and artist-heralds most likely employed colorants imported from Europe.[30] There were long-established and complex marine trade routes with Britain, France, the Iberian Peninsula and the Netherlands. In spite of trade being greatly disrupted by rebellions and civil wars during the 17th century, an increase in imported consumer goods continued across the country.[31] The port books of Bristol, Ulster, Chester and London provide evidence that colorants, as well as other painting and drawing materials, were imported into Ireland at this time. The following materials are mentioned: verdigris, red lead, vermilion, lead white, yellow ochre as well as alum and dyes such as saffron, orchil, madder, woad, indigo, brazilwood, indigo and logwood; ink, including the ingredients to make it and tools to use it (inkhorn, galls, copperas, penners); and paper, likely from France and Italy.[32]

As in other European cities, colorants were sold by Dublin merchants and apothecaries, as many pigments were used as both medicinal cures and painting materials.[33] In the excavation of a 17th-century site in Dublin city, yellow arsenic sulphide was found within pottery artefacts[34] linked to an apothecary's shop that may have belonged to a Dutchman called Jacob Ryckman.[35] Dutch merchants settled in Dublin and records show that in 1611, direct trade of provisions from the Netherlands included colorants such as madder and indigo.[36]

Table 2 Comparison of the colorant materials identified in the NLI heraldic manuscripts analysed with published examples of western European illuminated manuscripts dated to the 16th and 17th centuries.

Colorants	Irish GO MS series	Tudor maps of Ireland	Portuguese MSS	Spanish MSS	Old Slavonic MSS	German MSS	Import records into Ireland	Limning treatises 16th–17th century
Azurite/blue verditer	X	X	X	X	X	X		X
Indigo/woad	X	X			X		X	X
Ultramarine						X		X
Smalt	X	X		X				X
Cinnabar/ vermilion	X	X	X	X	X	X	X	X
Red lead	X	X			X	X	X	X
Realgar								X
Red ochre								X
Red lakes	X	X	X	X	X	X	X	X
Organic purples (orchil…)		X	X			X	X	X
Indigo mixtures for purples			X					
Arsenic sulphide yellows (orpiment)	X	X			X	X		X
Yellow ochre			X				X	X
Lead based yellows (lead-tin yellow, massicot…)			X					X
Yellow lake	X	X	X				X	
Gold	X	X	X		X			X
Cu-based green (verdigris, malachite/ green verditer)	X	X	X	X	X	X		X
Green earth				X				
Sap green								X
Vergaut	X							
Azurite +yellow	X	X		X				
Brown ochre, umber		X	X					X
Calcium-based white	X			X				
Lead white			X	X			X	X
Bare paper	X	X			x			
Calcium- based black	X		X					X

The current body of literature on both the materiality of Irish heritage[37] and pigment identification in heraldic manuscripts is limited.[38] A comparable collection of English heraldic manuscripts exists in the College of Arms (London), but scientific analysis on material from this timeframe has yet to be undertaken.[39] The palette of colorants found on western medieval manuscripts has been well defined in recent years.[40] Parallels of use of colorants can be found with Tudor easel paintings[41] and miniatures.[42] Therefore, to gain context, the colorants identified in NLI's heraldic manuscripts were compared with the published results of analyses of other 16th- and 17th-century manuscripts in western Europe. These included: a corpus of 15 manuscript maps produced by eight English cartographers working in Ireland during the late 16th and early 17th century;[43] heraldic designs of 16th-century Portuguese charters[44] and 17th-century Portuguese illuminated manuscripts;[45] a group of 17th-century Spanish choir books;[46] two German medical treatises dated 1524–50 and 1675;[47] and a series of Old Slavonic manuscripts dated to the 16th and early 17th century.[48] As shown in Table 2, the materials identified in the Irish heraldic manuscripts are in line with the palette employed in contemporary illustrated manuscripts across Europe, including the widespread use of colorants such as azurite, indigo, vermilion, red lead, red and yellow lakes and copper-based greens.

Conclusion

Three rare 17th-century Irish manuscripts with heraldic illuminations on paper (NLI's GO MS 44, 46 and 64) were investigated using non-invasive analytical techniques. The full palette of colorants, their mixtures and painting techniques were characterised. The use of colorants varied slightly in the different manuscripts analysed and correspond to different artist-heralds at work over a 50-year period. A comparison of the results with contemporary written sources and technical analysis of other European illuminated manuscripts shows that the artist-heralds working in Dublin painted with similar artistic techniques and materials found in other centres of artistic production. A review of primary sources on Irish trade in the 17th century indicates that colorants were imported through several Irish ports, and their availability followed European market trends.

This is the first time that colorants on Irish heraldic manuscripts from the 17th century have been analysed and documented. The material evidence from this study sits at the intersection of trade/economic history, art history, conservation and heritage science. This paper contributes to broader cross-disciplinary discussions of material culture and the trade of luxury goods to an island nation at a time of enormous political and cultural change. As there are few surviving examples of artistic production in early modern Ireland, this research will help build a framework for the comparison and contextualisation of the materiality of cultural heritage artefacts produced in Ireland in the 16th and 17th centuries.

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Notes

1. Butler 2012. Many of the manuscripts (GO MS series) are digitised and accessible on NLI's online catalogue: https://catalogue.nli.ie/.
2. J. Dorney, 'The Eleven Years War 1641–52 – A Brief Overview – The Irish Story', Available at: https://www.theirishstory.com/2014/01/10/the-eleven-years-war-a-brief-overview/ (accessed 30 November 2024).
3. The collection 'narrowly escaped' transfer to the Public Records Office just prior to its destruction: 1922: 45. See also the Virtual Record Treasury of Ireland, https://virtualtreasury.ie/the-1922-fire (accessed 30 November 2024)..
4. Woodcock and Robinson 1988: 50–54.
5. Roland 2014; Goldring 2015.
6. MacCarthy 1996: 37.
7. MacCarthy 1996: 189. Molyneux travelled from Dublin to the London court to collect ceremonial robes in 1612.
8. McGrath 2021: 66.
9. Tait 2002: 40–48; Goldring 2015; Hiltmann 2017.
10. Woodcock and Robinson 1988: 50–54.
11. Pereira-Pardo et al. 2023.
12. Caffrey 2014: 58.
13. Hoysted 2016.
14. The folios were examined with transmitted light. In GO MS 44 a partial beehive watermark is visible, in GO MS 46 a faint fleur-de-lis watermark is present, and in GO MS 64, a partial watermark, possibly of grapes, is present. See O'Connor 2022 for a general discussion on sources of paper in the NLI heraldic manuscripts collection.
15. Leica M80 stereomicroscope with Leica MC170 HD digital camera, on LAX software and a Dino-Lite Edge and AM 4000 portable USB microscopes using Dino Capture 2.0 software.
16. FORS was used to determine the molecular composition of the materials, including some organic dyes. FORS was done with a Labspec4 instrument (ASD), which has a spectral resolution of 3 nm (at 700 nm) and 10 nm (at 2100 nm). 30 scans were acquired and averaged per spectrum. A bifurcated reflectance probe and an external tungsten-halogen light source (HL-2000-HP-FHSA by Ocean Optics) were used, the latter with an attenuator and a VIS bandpass filter (Thorlabs) to keep the illumination on the sample below 1250 lux and 25 W/cm^2, as recommended to minimise the risk of light-induced damage and ensure a negligible heating of the sample. Indico-pro and Spectrograph software were used for spectra acquisition and analysis. Problem spectra obtained from the illuminations were compared with reference spectra acquired on in-house paint mock-up samples or those available on online databases

(IFAC-CNR n.d.) and published in the literature. To ease interpretation, a spectrum of the blank substrate was always taken and overlaid to the pigments' spectra, to understand the contribution of the base paper.

17. pXRF analysis showed the elemental composition of inorganic components of the illuminations, such as metals, some inks and mineral and synthetic inorganic pigments. A XL3t-Ultra handheld instrument (Niton) was used, in the mining mode (Cu/Zn), with a 3 mm diameter spot size and 60–80 s acquisition time, automatically changing filters and conditions for the detection of main (40 kV, 50 μA) and light elements (15 kV, 100 μA). NDT and Artax (Bruker) software were used to capture and process the spectra. Results from a previous analytical study carried out in collaboration with the National Gallery of Ireland using a pXRF Bruker S1 Titan instrument were also revisited.
18. Odlyha et al. 2000; Frost et al. 2002; Mattei et al. 2008; Coccato et al. 2017: 12–13.
19. Kirby 1999: 31, 35; Berrie 2015: 312–22.
20. Coccato et al. 2017: 16–17: Biolcati et al. 2023: 5406.
21. Pereira-Pardo et al. 2023: 206.
22. Coombs 2009: 81.
23. Harley 1982: 12; Muller and Murrell 1997: 15.
24. Murrell 1993/94: 2.
25. Peacham 1612: 69–82.
26. Muller and Murrell 1997: 59–62.
27. Murrell 1993/94: 36.
28. Plender 2015: 124–5.
29. McGrath 1975: 330. Azurite was mined in Tipperary. Natural colorants from local organic materials may have been available.
30. Kirby 2019.
31. Gillespie 2009: 60.
32. Flavin and Jones 2009; Flavin 2014; O'Connor 2022; Hunter 2012: 2–11.
33. Nurse 2021.
34. A. Hayden, personal communication, 20 August 2019.
35. Cunningham 2016; Hayden 2018: 17.
36. Loeber 1981: 74.
37. Scientific analysis of the materiality of Irish heritage is an emerging area of research. Colorants present on medieval insular manuscripts housed in the library of Trinity College Dublin have been analysed (see Bioletti and Moss 2017). Very few illuminated Irish manuscripts from the 12th to 16th centuries still exist (see Moss 2015), and scientific research on their inks is in progress (see Biolcati et al. 2023).
38. Huxtable 2002:14; Adams 2014: 354.
39. Christopher Harvey, Head of Conservation, College of Arms (London), personal communication, 1 March 2023.
40. Burgio et al. 2010; Ricciardi and Rose-Beers 2016; Panayotova 2020; Gameson et al. 2023.
41. Plender 2015: 122.
42. Fiorello et al. 2021: 1168–78.
43. Pereira-Pardo et al. 2023: 204–7.
44. Barrosa et al. 2018: 387.
45. Le Gac et al. 2013: 243.
46. Bueno Vargas et al. 2006: 151–9.
47. Nurse 2021: 98–9.
48. Nastova et al. 2015.

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