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University of Durham

December 2021

Illuminating the past: A spectroscopic examination of the artwork in seven French thirteenth-century manuscripts

Department of Chemistry and Department of History

This thesis is submitted in fulfilment of a doctorate

"To read the historical record, it's sometimes not enough to look at the page - you have to look through it and behind it."

Hilary Mantel, on the scientific analysis of manuscripts, 2020.

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Abstract

Illuminated medieval manuscripts can be exquisitely decorated and extremely valuable. Whilst close investigation of the artwork contained is necessary for conservation, art-historical and historical information, only non-invasive and non-destructive techniques that can be carried out *in situ* are appropriate.

This thesis details the techniques employed at Durham University to analyse the pigments and dyes found in such manuscripts, along with the latest scholarship in the field and in the history of pigment production and use. An overview of the field of codicology, the study of the production of manuscripts, is provided, alongside an introduction to how scribes and illustrators prepared and produced illuminations.

The use of technology and the history of manuscript manufacture and illustration are combined in a series of case studies. The codicology and artwork of a group of seven thirteenth-century Bibles, mainly from Paris, are explored and their colourants identified. New data from the analysis of the pigments enhances and extends existing scholarship in the field of scientific manuscript analysis.

This research lies at the intersection of science, history, and artistic practice.

Durham University

2021

Dedication and Acknowledgements

For Florence and Leo

Starting a doctorate, in 2016, when my daughter Florence was just five months old was never going to be easy, and things became further complicated still - in a good way - when Leo was born in 2018. I foresaw interesting times ahead, but I couldn't perhaps have foreseen just how 'interesting' things were going to get – with a pandemic and a military coup! There were times when sitting down to write this thesis was a balm, and times when it seemed as if finishing a PhD was just a step too far. I'm proud to say that my dogged determination saw it through.

However, none of that could have been possible without the help and support of numerous people. My supervisors, Professor Richard Gameson (History) and Professor Andrew Beeby (Chemistry) have been a constant source of guidance, help, support, and humour. Early on in my doctorate Dr Elizabeth Archibald also provided many interesting and useful ideas. So many of the staff at Palace Green Library have also been so helpful to me along the way.

I am grateful to the Centre of Visual Arts and Cultures, and The Leverhulme Trust, for the funding and training provided for me to undertake this doctorate. A very large thank you must go to Professor Ludmilla Jordanova for her help, support, and encouragement over the years, especially during the early stages of the pandemic, when things seemed very bleak.

Being part of the Leverhulme Doctoral Programme at Durham ensured I had a ready-made support network, and I would like to thank them all for the humour, help and inspiration that they have provided. I would also like to mention Andrei Markin and Barbara Hargreaves everything they have done for me.

Last but certainly not least, I would like to thank my long-suffering family for everything they have done. My parents have provided endless childcare, driving up and down the country to lend their aid. My partner Matt has done so much to support me that a mere sentence in an acknowledgement will never be enough to show my appreciation. Finally, I'd like to mention my children, Florence and Leo, who are disappointed that the 'book' I have been writing isn't a bed-time story, but who have inspired me to keep me going in innumerable ways. All my love.

Acronyms and Abbreviations

General Terminology

AHRC	Arts and Humanities Research Council
BCE	Before Common Era
CE	Common Era

Libraries

BOD	Bodleian Library Oxford
CCCC	Corpus Christi College Cambridge
DCL	Durham Cathedral Library
DUL	Durham University Library
JRL	The John Ryland's University Library, Manchester
LPL	Lambeth Palace Library
NCO	New College Oxford
SJCC	St. John's College, Cambridge
TCC	Trinity College, Cambridge
TCD	Trinity College, Dublin
TCO	Trinity College, Oxford
UUB	Uppsala Universitetsbibliotek

Scientific Terminology

ATR	Attenuated Total Reflection
CIELab	Commission Internationale de l´Eclairage L*a*b*
DRIFT	Diffuse Reflectance Infrared Fourier Transform
EM-CCD	Electron Multiplying Charged Coupling Device
ER	External Reflection
FORS	Fibre-optic Reflectance Spectroscopy
FTIR	Fourier Transform Infrared
IR	Infrared
L*a*b*	Lightness, a-value, b-value
MA-EDXRF	Macro Energy Dispersive X-Ray Florescence
MA-rFTIR	Macro reflectance Fourier Transform Infrared
NIR	Near Infrared
RGB	Red, Green, Blue
RIS	Reflectance Imaging Spectroscopy
RTI	Reflectance Transformation Imaging
SWIR	Short-Wave Infrared
UV	Ultraviolet
Vis	Visible
XRF	X-Ray Florescence

Papers published

The following papers have been developed during the lifetime of this doctorate. L. Garner is mentioned either as a co-author or 'with the assistance of':

- Beeby, Andrew, Louise Garner, David Howell, and Catherine E. Nicholson. "There's More to Reflectance Spectroscopy than Lux'. *Journal of the Institute of Conservation*, 8 May 2018, 1–12.

- Gameson, Richard, Giorgia Marucci, Andrew Beeby, Louise Garner, and Catherine Nicholson. 'The Colour of the Law'. *Codices Manuscripti et Impressi*, no. 112/113 (2019).

- Gameson, Richard, Andrew Beeby, Catherine E. Nicholson, and Louise Garner. 'Late Medieval English Illuminators' Blues'', forthcoming.

- Gameson, Richard, Andrew Beeby, Catherine Nicholson, and Louise Garner. 'Les Cent Nouvelles Nouvelles: The Physical Fabric of the Fables', forthcoming.

In addition, L. Garner is credited with assisting with the pigment identification work in the book:

- Richard Gameson, *Literature and Devotion in Later Medieval England* (Durham: Sacristy Press, 2021).

Chapter One

Introduction and Relevant Scholarship

Introduction

Context

Illuminated medieval manuscripts hold a particular fascination for historians, literary scholars, and everyday people alike. The most talented scribes, artists, and bookmakers of centuries past collaborated on these fabulous volumes to create some of the most exquisite artefacts known to man. These manuscripts would have been highly prized and cherished in their own day, and their survival into the modern day renders them priceless and irreplaceable. As a testament to their popularity, the field of manuscript studies in universities and cultural institutions is thriving.

However, the qualities that make historic manuscripts so interesting to study - their fascinating provenance, their age, irreplaceability, and cultural significance - are also the qualities that can make examining them so difficult. Often manuscripts are fragile - they may not open very well, and the leaves may not stay flat for close and easy inspection. There are strict rules for the handling and display of most manuscripts, as conservators are keen to minimise exposure to light and humidity, and any methods intended for the analysis of the materials employed must be non-contact, non-invasive and leave no lasting mark: certainly, within the United Kingdom sampling is forbidden. Due to their fragility, high value and thus high insurance costs, or the complex nature of bequest, acquisition, and archival storage, manuscripts cannot usually be moved from their home repository.

Despite these difficulties, the interdisciplinary field of manuscript studies is vast. Whilst it can be useful to examine, say, a splendid lectionary in isolation - commenting on the beautiful artwork, text, and script - one manuscript is part of a much wider scene that should also be studied in order to properly put the work in context. The production of manuscripts hints at large networks - of the people who read, edited and glossed their books - of personal patronage, prayer, and devotion - of a thriving trade in parchment, tools, and pigments - and of the associated farmers and tradesman, guilds, toolmakers, and their industry. Each manuscript sits at the centre of a vast network that lies waiting to be discovered, and the analysis of pigments, their manufacture, provenance, and their trade routes, is a crucial part of this.

In the past few centuries, various scientific techniques have been employed to understand further the technology employed in making these books. At first, the field was invasive - samples were taken, books were unbound, and parchment was cut. Some nineteenth-century scholars even employed a method of staining the surface of the parchment with a reagent, in one case using strongly brewed tea, in an effort to reveal the secrets that lay beneath erasures: such as that was inflicted by C. Maier on the Vercelli Book.[1] However, these techniques have thankfully been recognised as damaging and detrimental, and most institutions now forbid the sampling or invasive investigation of their work. Fortunately, there are now an increasing number of non-invasive analytical scientific techniques that can be employed. As the technological capability to investigate manuscripts closely and non-invasively has advanced greatly in recent years, the research and discussion in this area have burgeoned to provide fresh insights into scribal practices of the past.

One area of manuscript studies that has benefitted immensely from this analysis is the study of the inks and pigments used to write and decorate these great works. In the field of history, knowledge of which pigments were used to create illustrations can answer many questions. Individual illuminations and other artworks can be assigned to individual scribes or illuminators. Knowledge of scribal practice can tell us more about how manuscripts were created, the transmission of manuscripts across the world, and the itinerary of scribes/illuminators. Trends in pigment use over time and place can show the emergence of, and changes to, trade routes, and the interrelations of cultural events and commerce can be perceived.

Aside from this material history, pigment analysis also has many conservation implications, as the correct identification of colourants allows appropriately targeted conservation techniques to be applied. There are also wider applications of pigment and dye identification, for example, to detect later interventions where anachronistic paints are employed.

As the application of non-invasive analytical techniques on priceless manuscripts has become more commonplace, an increasing number of scholars are turning to science to answer the questions they are asking, and technology has had to keep pace to provide the answers. At the University of Durham, the capabilities of the Raman spectrometer that occupies an entire room and weighs half a ton are replicated by a portable spectrometer that fits into a suitcase. Advances in portability mean that the equipment can travel nationally and internationally to a manuscript, and examination can occur *in situ* rather than the manuscript having to move.

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[1] Oliver Bock, 'C. Maier's Use of a Reagent in the Vercelli Book', *The Library* 16, no. 3 (September 2015): 249–81

Alongside advances in technology are advances in researchers' interpretations and capabilities. Scientists are becoming more adept at using ever lower-powered lasers and light to identify samples, enhancing scientific knowledge and skills whilst respecting good conservational protocols. Whilst parchment manuscripts are not particularly fragile, their bindings often are, and their illustrations may also be vulnerable. Past exposure to sunlight, water damage, rough treatment, and the passage of time itself can degrade the pigment colour or composition, or both; equally pigments sometimes flake off the writing support. Sometimes pigments can 'eat' through the parchment itself or react with other pigments to produce unfavourable effects. Conservation research, aided by details such as that contained in this study, aims to halt this.

Questions

This thesis aims to analyse and report on the artworks contained within seven thirteenth-century bible manuscripts made in France or southern England and, therefore, draws on the two disciplines of science and history. In so far as these manuscripts have been scrutinised before, this has been through a paleographical, historical, art-historical or text-based lens and not via scientific analysis. Furthermore, this collection of manuscripts, chosen on account of commonalities of content, date and/or place of manufacture, has never been considered together as a corpus. This thesis, therefore, aims to advance knowledge and build upon previous scholarship by incorporating pigment identification into the analysis of them. As very few northern French and southern English manuscripts of the thirteenth century have had their pigments analysed, the present work addresses a real lacuna in current knowledge.

Approach and methodology

Following this introduction, the second section of this chapter is an overview of pertinent scholarship. Firstly, the field of the scientific study of manuscripts, with a particular focus on pigment analysis, is discussed. Crucial past studies and the work of relevant current leaders in the sphere are examined. Secondly, the most relevant scholarship concerning Paris Bibles and thirteenth-century northern European manuscript manufacture is reviewed. This exploration provides the context amongst which this thesis, its aims, and its discoveries are situated. Finally, this chapter situates the work that Team Pigment undertake within this milieu. It is under the auspices of Team Pigment that this study is conducted.

The second chapter provides an overview of the typical and atypical pigments and dyes used in manuscript production in the period examined and investigates the manuscript recipe books that were likely in circulation in northern France and southern England at the time and thus would likely have

formed part of the written scholarship of knowledge of pigment and dye production. The methods of manuscript creation are also briefly examined as it is by understanding how manuscripts were made that we can appreciate the labour that went into creating their artworks.

In the third chapter, the various scientific techniques used to analyse pigments are discussed, with an in-depth survey of the technology and equipment utilised at Durham University, and thus in this thesis.

Chapter Four contains a detailed study of seven thirteenth-century bible manuscripts, with a comprehensive analysis of their codicology, artwork, and pigment use. This fourth chapter is split into three sections of roughly equal length for the ease of the reader. The first provides an overview of the Paris bible "genre" and reports the analysis undertaken on DCL A.II.3 and DUL Cosin V.v.17. The second section details the data gathered from DUL Cosin V.v.18, DCL A.IV.30 and DCL A.IV.37, and the third section reports on the findings from NCO 1 and NCO 20, as well as a conclusion that discusses the results and analysis of the entire corpus.

Citations

The citation style followed here is that of the Humanities, wherein journal titles are generally given in full.

Nomenclature of Manuscripts

Manuscripts are usually referenced by their library and shelfmark and sometimes by a common name, which relates to its text, location, or provenance. I have tried to give both where appropriate. Where manuscripts are repeatedly referred to, after the first introduction, the library name is dropped. A list of commonly abbreviated library names (and other abbreviations) can be found on page 6.

Manuscripts are normally foliated, not paginated – i.e., it is the leaves, not the pages, that are numbered. Thus, the first page is folio 1 recto (usually and hereafter referred to as fol. 1r), and the second page (the reverse of the same leaf) is folio 1 verso (hereafter referred to as fol. 1v). The third 'page' would be fol. 2r, the fourth (the verso of the second leaf) fol. 2v and so on. Citing foliation in medieval manuscripts is often tricky due to missing leaves or past incorrect numbering etc., so the commonly understood folio number is used here, even if strictly the numbering may be inaccurate.

Manuscripts are commonly dated using roman numerals where, for example, 's.x' indicates a tenth-century manuscript 's.xi' an eleventh and so on. 's.' stands for the Latin *saeculo,* which means 'in the age'. Further conventions include:

- s.x^{1} means the first half of a century (here 900-950)
- s.x^{2} means the second half of a century (here 950-1000)
- s.x^{in} means the first quarter of a century (here 900-925)
- s.x^{ex} means the last quarter of a century (here 975-1000)
- s.x^{med} means the middle two quarters of a century (here 925-975)
- s.ix^{ex} – s.x^{in} indicates the turn of a century (here 875-925)
- c.900 indicates an approximate date

In this study, I have tried to avoid these shorthand definitions. However, in most of the literature cited, these conventions are commonly followed, so an explanation is appropriate.

Use of commercial pigments

Pigments used as reference samples in this study have been sourced from either Kremer Pigmente in Germany or Cornelissen in London unless otherwise stated.

Use of binders

A binder is a medium in which a pigment, often in powdered form, is held in order to "stick" it to the page. Binders are discussed in more detail in Chapter Two. For the reference samples prepared for this study, commercially available gum Arabic was used when preparing paints, and free-range hen's eggs from local shops were used for tempera binding.

Scientific and Technical Conventions

Technical conventions, such as calibration error and background removal in Raman spectra, are discussed more fully in Chapter Three, alongside the technical and scientific explanations of the systems and procedures used.

Acronyms

As with acronyms of library names, scientific techniques are similarly used in full in the first instance and then abbreviated thereafter. A full list of acronyms can be found on page 6.

Limitations and Errors

It would be remiss and remarkable not to mention the impact that the Covid-19 pandemic has had on this study. Although the bulk of data was collected before March 2020, it is clear that missing data,

erroneous spectra, and potentially data on one or two other manuscripts could have been collected were libraries not closed from March to October 2020 and then again from November to Spring 2021.

Were I to start this project again, I would certainly be more discerning about the spectra taken to avoid large amounts of duplicate or unnecessary data. Conversely, I would have been more methodical in ensuring I had all the data I needed from each page – a methodology I developed as I became more proficient in my data collection. In addition, I would have taken advantage of the multispectral imaging equipment more, as there are some manuscripts in this study that have not benefitted from that analysis.

Collection of Data

Prior to March 2020, all data were collected by me, closely supervised by either Prof. Andrew Beeby (Durham University) or Dr Kate Nicholson (Northumbria University), who monitored the safe use of scientific equipment, and Prof. Richard Gameson (Durham University), who monitored correct manuscript handling. These data form the bulk of this thesis.

As the pandemic curtailed my access to the manuscripts, further data were kindly collected by Prof. Andrew Beeby and Prof. Richard Gameson in December 2020 and subsequently analysed by me. This consisted of:

- Fibre-Optic Reflectance Spectroscopy (FORS) on three folios of DUL Cosin V.v.18
- FORS on DCL A.IV.37
- Some additional multispectral imaging on DCL A.II.3

Relevant Scholarship

Context

Researchers have always sought to understand the process of manuscript manufacture and the skills, tools and components employed. Written sources, modern recreations and codicological studies have provided much information for the art-historian, but as mentioned, recently, the field has seen many further advances with the employment of science and technology.

As this thesis aims to integrate research from both science and history, conventions from both must be considered. Therefore, a review of pertinent historical sources and scholarship will read slightly differently from a scientific or technical scholarship review. This difference is perhaps best encapsulated by a quote from DJ De Solla Price in a methodological research paper that tries to unpick

these differences, "[The humanities] has a humanistic type of metabolism in which the scholar has to digest all that has gone before, let it mature gently in the cellar of his wisdom, and then distil forth new words of wisdom about the same sorts of questions. In hard science, the positiveness of the knowledge and its short term (sic) permanence enable … to emerge at the research-front where interaction with one's peers is as important as the storehouse of conventional wisdom".[2]

In practice, this means that in this thesis, the appraisal of scholarship in the scientific arena concentrates on more recent endeavours, with most of the scholarship dating from recent years, and thus considered to be at the 'research-front', plus only such older work as is deemed seminal. Many papers are published in research groups with many contributors. In contrast, the survey of works distilled from the field of history takes in a longer time span, and the scholarship contains works by noticeably fewer authors. In one of her most recent publications, Stella Panayotova laments the difficulties of grappling with older literature in the field of scientific manuscript analysis. She indicates that many studies published are somewhat hidden away in scientific journals, with many earlier studies offering only scientific and not art-historical analysis, and thus much of this work is not widely considered in art-historical or wider cultural studies. [3]

Scholarship in the Field of Scientific Analysis of Manuscripts

The history of scholarship in this field might be defined by original medieval source material and later modern scholarship. Original sources are those medieval treatises and manuscript recipe collections that detail pigment and dye collection, refinement and manufacture. Following these medieval sources were efforts in the late nineteenth and early twentieth century to curate, investigate and replicate the aforementioned recipes, leading to attempts in the last century to compare the appearance of replicated pigments with those in manuscripts and identify what had been used. These endeavours, plus relevant pre-2000 works, are considered briefly below, but moreso in Chapter Two - whereby recipe texts and treatise and early efforts at pigment identification are discussed in detail.

After this era, science and technological advancements beyond the microscope allowed for increasingly accurate pigment and dye identification, and below is a selected summary of these efforts since 1997. This date was chosen as the beginning for inclusion in this study as it is the date when

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[2] Thomas Franssen and Paul Wouters, 'Science and Its Significant Other: Representing the Humanities in Bibliometric Scholarship', *Journal of the Association for Information Science and Technology* 70, no. 10 (2019), p. 1129.

[3] Stella Panayotova, ed., *Scientific Analysis of Illuminated Manuscripts: A Handbook* (Harvey Miller, 2020), p. 12.

Robin Clark published the first Raman spectroscopy pigment library, occasionally utilised in this study, providing a baseline for Raman spectroscopic cultural heritage studies.

It would be very confusing to list the scholarship in this section in date order - as mentioned above, publications in scientific arenas can be prolific. Instead, the major publications by the foremost research groups that concentrate on pigments analysis of Western Manuscripts are detailed below, arranged by research group.

Pre-1997

Merrifield

A mid-nineteenth-century scholar, Mrs Merrifield, published *Original Treatises dating from the XIIth to XVIIIth Centuries on the Arts of Painting* in 1849. This text, examined further in Chapter Two, has remained a core text in the field as a starting point for further investigation of pigment and dye recipes.[4]

Thompson

Daniel Thompson (d. 1980) was a prolific researcher in the field of medieval pigments and published numerous studies on the subject that often form a basis for today's enquiry. His overview *The Materials and Techniques of Medieval Painting* is probably his best-known work.[5]

Roosen-Runge

In his day, Roosen-Runge was a pioneer and expert in pigments in Medieval manuscripts.[6] Working in the 1950s and 60s, he considered many important manuscripts in the light of experiments on pigments recreated from recipe collections. He was able to make highly-educated guesses as to the

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[4] M. P. Merrifield, *Original Treatises: Dating from the XIIth to XVIIIth Centuries on the Arts of Painting, in Oil, Miniature, Mosaic, and on Glass; of Gilding, Dyeing, and the Preparation of Colours and Artificial Gems; Preceded by a General Introduction; with Translations, Prefaces, and Notes* (J. Murray, 1849); Mary P Merrifield, *Original Treatises on the Arts on Painting Volume 2* (New York: Dover Publications, 1967).

[5] Daniel V. Thompson, *The Materials and Techniques of Medieval Painting* (New York, NY: Dover Publ, 1956).

[6] Mark Clarke, 'Really Don't Trust Your Eyes to Identify Manuscript Pigments!', *Gazette Du Livre Médiéval* 44, no. 1 (2004), p. 50.

identification of pigments, including those deployed in the Lindisfarne Gospels, using the only technology available to him at the time – a microscope.[7] His work is further examined in Chapter Two.

Post-2000 - Research Groups

MINIARE

The MINIARE project at The Fitzwilliam Museum, Cambridge, aims to "develop a comprehensive protocol for the non-invasive analysis of artists' materials and techniques." Recent initiatives from the project included a major exhibition of illuminated and illustrated manuscripts at The Fitzwilliam Museum, Cambridge, combined with an academic conference held in Cambridge in December 2016 – 'Colour: The Art and Science of Illuminated Manuscripts'.[8] This brought together the leaders in the arena of manuscript analysis for a once in a generation discourse that married the field of art history with science and technology.

A comprehensive catalogue of the exhibition with introductory notes for each item, presented thematically, was published before the conference. This provides a complete introduction to scientific and art historical analysis within an historic context. Following the three-day symposium, three further volumes were published. Two of these publications contained proceedings of the conference, and subsequently, there followed a handbook that expanded on themes investigated and presented six essays and fifty-eight detailed case studies of manuscript analysis. These publications were:

- Colour: The Art and Science of Illuminated Manuscripts [9]
- Manuscripts in the Making: Art & Science Volume One [10]
- Manuscripts in the Making: Art & Science Volume Two [11]
- Scientific Analysis of Illuminated Manuscripts: A Handbook [12]

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[7] Roosen-Runge, H.; Werner, A. E. A., "The pigments and medium of the Lindisfarne Gospels." In: T. D. Kendrick (ed.) Evangeliorum Quattuor Codex Lindisfarnensis, OltunLausanne: Urs Graf Verlag, 1960, II.l.V.I, pp. 261-295

[8] Stella Panayotova et al., eds., *Colour: The Art & Science of Illuminated Manuscripts* (London Turnhout: Harvey Miller Publishers, 2016).

[9] Panayotova et al., *Colour*.

[10] Stella Panayotova and Paola Ricciardi, eds., *Manuscripts in the Making: Volume One*, vol. One, Two vols (Harvey Miller, 2017).

[11] Stella Panayotova and Paola Ricciardi, eds., *Manuscripts in the Making: Volume Two*, vol. Two, Two vols (Harvey Miller, 2017).

[12] Panayotova, *Scientific Analysis of Illuminated Manuscripts*.

At the 'Colour' conference, and subsequently published in the conference proceedings, Stella Panayotova, Lucia Pereira-Pardo and Paola Ricciardi presented preliminary findings of FORS and XRF analysis conducted on twelve fourteenth-century English manuscripts, which centre around the Queen Mary Psalter (BL, MS Royal 2 B. VII) dated to the 1310s.[13] Another paper resulting from the conference, by MINIARE, explored technical details regarding how MA-XRF scanning is employed to analyse illuminations. Employing this technique on three manuscript cuttings allowed elemental distribution maps to be created, although in many cases, it was crucial to combine the results with those from MA-rFTIR scanning for accurate analysis. More information on the techniques of elemental analysis (XRF) and reflectance spectroscopy (rFTIR) are provided in Chapter Three.[14]

Further papers published in the proceedings by MINIARE included a study on the Psalter-Hours of Isabelle of France, a paper entitled *The Use of Copper Sulphates in Sixteenth-Century Flemish Illumination: Simon Bening as a Case Study* and another titled *Painting materials in the Fitzwilliam Book of Hours: new discoveries*.[15] In the latter, a Book of Hours painted c.1515 was examined with infrared imaging, optical microscopy and reflectance spectroscopy in the UV-Vis-NIR-SWIR range and, in collaboration with Team Pigment at Durham University, was also analysed with FTIR and Raman spectroscopy. Subsequent analysis revealed the deployment of unusual pigments for the time and place, including a clay-rich ochre and a green copper sulfate, as well as clarifying the role played by the main artists and other painters in the creation of the book.[16] In the handbook, an essay - *Science of the Book* - was included.[17]

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[13] Panayotova and Ricciardi, *Manuscripts in the Making: Volume Two*, pp. 47-64.

[14] Stijn Legrand, Paola Ricciardi, and Koen Janssens, 'The Benefits of Scanning Illuminated Manuscripts with MA-XRF and MA-RFTIR', in *Manuscripts in the Making: Art and Science*, vol. two (London and Turnhout: Harvey Miller/Brepols, 2017), p. 169.

[15] Stella Panayotova, 'The Psalter-Hours of Isabelle of France in the Nineteenth-Century', in *Manuscripts in the Making: Art and Science*, vol. two (London and Turnhout: Harvey Miller/Brepols, 2017), p.182-190; Paola Ricciardi and Stella Panayotova, 'Painting Materials in the Fitzwilliam Book of Hours: New Discoveries', in *Manuscripts in the Making: Art and Science*, vol. one, two vols (London and Turnhout: Harvey Miller/Brepols, 2017), pp. 144-155; Paola Ricciardi and Giulia Bertolotti, 'The Use of Copper Sulphates in Sixteenth-Century Flemish Illuminations: Simon Bening as a Case Study', in *Manuscripts in the Making: Art and Science*, vol. two (London and Turnhout: Harvey Miller/Brepols, 2017), pp. 118-131.

[16] P. Ricciardi and S. Panayotova, Painting materials in the Fitzwilliam Book of Hours: New Discoveries, in S. Panayotova and P. Ricciardi (eds.), *Manuscripts in the Making: Art and Science vol. 1, Harvey Miller/Brepols*, London and Turnhout, 2017, p. 152

[17] P. Ricciardi and C. Schmidt Patterson, Science of the Book, in S. Panayotova (ed.), *A Handbook of the Art and Science of Illuminated Manuscripts*, Harvey Miller/Brepols, London and Turnhout, 2020, 35-71

In addition, a thematic collection of papers was published in *Heritage Science* in 2019, which derived largely from the posters presented at the conference with an editorial by Ricciardi. Included in this was a paper with Ricciardi as co-author entitled *Non-invasive identification of paint binders in illuminated manuscripts by ER-FTIR spectroscopy.*[18] This study examined how successful differing methods of FT-IR (ATR and ER) were at discriminating different binding mediums in paint outs and in real works of art. The study revealed that egg-based binders could be discerned from those that are gum Arabic-based and that carbonates hinder the identification of the binder.

Aside from this array of publications connected to the 'Colour' conference, the MINIARE project's latest journal articles include *A holistic, non-invasive approach to the technical study of manuscripts. The case of the Breslau Psalter*.[19] This paper details an integrated approach to manuscript study combining palaeographical, textual, historical, art-historical, and codicological analyses with data obtained from photomicroscopy, infrared imaging, visible and near-infrared reflectance spectroscopy, and X-ray fluorescence spectroscopy.

Ricciardi has recently published a collaborative paper with institutions in Florence - *'The Choir Books of San Giorgio Maggiore in Venice: Results of in Depth Non-Invasive Analyses.*[20] In this paper, the palette of ten of the choir books was assessed with UV-VIS-NIR FORS, Raman spectroscopy, XRF and microscopy. As well as discussing the difficulties and solutions of working with large, fragile volumes, the paper also details 'detection of unusual painting materials such as bismuth ink'. Furthermore, the paper reports that the palette discovered has prompted revision of the notion that one of the books was painted by a single illuminator.

Of particular relevance to this study is a paper published by Ricciardi et al. on the intentional use of calomel as a pigment in a fifteenth-century illuminated manuscript.[21] As mentioned in Chapter Two,

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[18] Luca Nodari and Paola Ricciardi, 'Non-Invasive Identification of Paint Binders in Illuminated Manuscripts by ER-FTIR Spectroscopy: A Systematic Study of the Influence of Different Pigments on the Binders' Characteristic Spectral Features', *Heritage Science* 7, no. 1 (December 2019): 7.

[19] P. Ricciardi and S. Panayotova, 'A holistic, noninvasive approach to the technical study of manuscripts. The case of the Breslau Psalter', in 'The Noninvasive Analysis of Painted Surfaces: Scientific Impact and Conservation Practice', Smithsonian Contributions to Museum Conservation, no. 5 (9 November 2016): 25-36

[20] Paola Ricciardi et al., 'The Choir Books of San Giorgio Maggiore in Venice: Results of in Depth Non-Invasive Analyses', *Heritage* 2, no. 2 (14 June 2019): 1684–1701.

[21] Mila Crippa et al., 'New Evidence for the Intentional Use of Calomel as a White Pigment', *Journal of Raman Spectroscopy* 52, no. 1 (2021): 15–22.

calomel is sometimes seen as a degradation product when cinnabar degrades. This paper reports the earliest use of calomel found to date.

Other recent publications by Ricciardi include a paper published with Christine Kimbriel titled *Secrets of a silent miniaturist: findings from a technical study of miniatures attributed to Isaac Oliver,* and *The importance of being little: MA-XRF on manuscripts on a Venetian island* along with several co-authors.[22] Ricciardi has also made a contribution to *The Encyclopedia of Archaeological Sciences* with John Delaney (see below), who is the senior imaging scientist in the conservation department at The National Gallery of Art, Washington, USA, entitled *Multispectral and hyperspectral imaging of artworks*.[23]

Spike Bucklow, also a member of MINIARE, is a scientist at the Hamilton Kerr Institute in Cambridge, whose publication "The Alchemy of Paint" examines the medieval palette.[24] The book delves into the alchemical and scientific background of pigments whilst also discussing the use and meaning of their colours.

One of the most recent publications from the MINIARE group is a contribution by Ricciardi to an edited volume *Spectroscopy, Diffraction and Tomography in Art and Heritage Science*, entitled *UV-visible-near IR reflectance spectrophotometry in a museum environment*.[25]

CHERISH

Another Fitzwilliam Museum research collaboration awarded AHRC funding in late 2020 is CHERISH (Cambridge Heritage Science Hub), which brings together a consortium of five Cambridge institutions - The Fitzwilliam Museum, The Hamilton Kerr Institute; the McDonald Institute for Archaeological Research; the Museum of Archaeology and Anthropology; and Cambridge University Library. Led by Paola Ricciardi, mentioned above, and Marcos Martinón-Torres, Pitt-Rivers Professor of

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[22] Christine Slottved Kimbriel and Paola Ricciardi, 'Secrets of a Silent Miniaturist: Findings from a Technical Study of Miniatures Attributed to Isaac Oliver', *British Art Studies*, no. 17 (30 September 2020); Anna Mazzinghi et al., 'The Importance of Being Little: MA-XRF on Manuscripts on a Venetian Island', *X-Ray Spectrometry*, 16 July 2020.

[23] Paola Ricciardi and John K. Delaney, 'Multispectral and Hyperspectral Imaging of Artworks', in *The Encyclopedia of Archaeological Sciences*, ed. Sandra L. López Varela (Hoboken, NJ, USA: John Wiley & Sons, Inc., 2018), 1–4.

[24] Spike Bucklow, *The Alchemy of Paint: Art, Science, and Secrets from the Middle Ages*, 1st ed (London ; New York: Marion Boyars, 2009).

[25] Paola Ricciardi, 'UV-Visible-near IR Reflectance Spectrophotometry in a Museum Environment', in *Spectroscopy, Diffraction and Tomography in Art and Heritage Science* (Elsevier, 2021), 103–31.

Archaeological Science at the Department of Archaeology, will be an interdisciplinary team that utilises scientific approaches to further understand cultural heritage.[26]

The Pigments of British Illuminators: A Scientific and Cultural Investigation

In collaboration with Team Pigment, MINIARE are undertaking a landmark study into pigments of the British Isles from the fifth to the fifteenth century. This project is described more fully under the Team Pigment section below.

Centre for the Study of Manuscript Cultures, University of Hamburg

The Centre describes itself as being 'engaged in fundamental research, investigating from both a historical and comparative perspective, based on material artefacts, the empirical diversity of manuscript cultures'.[27] The Centre publishes an annual journal, 'Manuscript Cultures'.[28] It has a dedicated library and graduate school and has close links with Kathmandu, Nepal, having an office there, allowing them access to Nepalese manuscripts. Recent publications of most relevance to this study include examinations of Tibetan-Buddhist manuscripts and work on the Berlin Turfan Collection.[29] [30]

Ira Rabin

Currently at the CSMC mentioned above, Ira Rabin has contributed to much scholarship regarding the history of ink, particularly in Egyptian works, and has analysed many texts which are known as 'The

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[26] Dr P. Ricciardi, 'CHERISH: Infrastructure for Research in Material Culture and Collections', Text, 30 November 2020, https://collectionsresearch.lib.cam.ac.uk/research-growth-networks/materiality/cambridge-heritage-science-hub/cherish-infrastructure.

[27]UMSC.'Manuskriptkulturen in Asien, Afrika Und Europa', accessed 16 December 2019, https://www.manuscript-cultures.uni-hamburg.de/.

[28] Universität Hamburg. 2009. Manuscript cultures: newsletter. Hamburg: Research Group Manuscript Cultures in Asia & Africa.

[29] Orna Almogi et al., 'Inks, Pigments, Paper : In Quest of Unveiling the History of the Production of a Tibetan Buddhist Manuscript Collection from the Tibetan-Nepalese Borderlands', *Journal of the International Association of Buddhist Studies*, 2013, 93–118.

[30] Desmond Durkin-Meisterernst et al., 'Scientific Methods for Philological Scholarship: Pigment and Paper Analyses in the Field of Manuscriptology', *Journal of Cultural Heritage* 17 (1 January 2016): 7–13.

Dead Sea Scrolls'. Two of her most recent publications, with others, include a paper on the evolution of inks in Egypt, and a publication and the scientific analysis of The Temple scroll.[31] [32]

MoLab

MoLab (Mobile Laboratories) is part of IPERION CH, which is a project funded by the European Commission. MoLab and partners have five centres located across Europe, which aim to provide facilities for *in situ* non-invasive measurements of artworks. Recent studies on manuscripts are varied in time and place, and include work on Mesoamerican codices, Persian manuscripts, and The Book of Kells.[33]

Other recent scholarship examined colour changes of Prussian blue in Danish paintings and an investigation of the pigments used in 'Sunflowers' by Van Gogh, in collaboration with the National Gallery (mentioned separately in this section).[34]

Lisbon Nova University

Lisbon University conservation and chemistry departments have published many wide-ranging papers in recent years on various aspects of pigment production, degradation, and use, from the medieval to the modern-day. One such paper, pertinent to this study, is entitled *Is a 1000-year-old mystery solved: Unlocking the molecular structure for the medieval blue from Chrozophora tinctoria, also known as folium.*[35] The study of purple colourants is one that is currently underway by several research groups, as, despite numerous examples of purple colours in books and even whole manuscripts coloured

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[31] Grzegorz Nehring et al., 'Looking for the Missing Link in the Evolution of Black Inks', *Archaeological and Anthropological Sciences* 13, no. 4 (April 2021): 71.

[32] Roman Schuetz et al., 'The Temple Scroll: Reconstructing an Ancient Manufacturing Practice', *Science Advances* 5, no. 9 (18 September 2019): 1–9.

[33] D. Domenici et al., 'Non-Invasive Investigations on Mesoamerican Codices: The MOLAB Approach', *Rendiconti Lincei. Scienze Fisiche e Naturali* 31, no. 3 (September 2020): 773–78; Chiara Anselmi et al., 'MOLAB ® Meets Persia: Non-Invasive Study of a Sixteenth-Century Illuminated Manuscript', *Studies in Conservation* 60, no. sup1 (August 2015): S185–92; B. Doherty et al., 'The Book of Kells: A Non-Invasive MOLAB Investigation by Complementary Spectroscopic Techniques', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 115 (November 2013): 330–36.

[34] Ella Hendriks and Marije Vellekoop, eds., *Van Gogh's Sunflowers Illuminated: Art Meets Science* (Amsterdam University Press, 2019); 'SUNMIX: Systematic Investigation of "Sunflowers" by Vincent van Gogh', *Iperion CH* (blog), accessed 28 May 2021, http://www.iperionch.eu/project/sunmix-systematic-investigation-of-sunflowers-by-vincent-van-gogh/.

[35] P. Nabais et al., 'A 1000-Year-Old Mystery Solved: Unlocking the Molecular Structure for the Medieval Blue from *Chrozophora Tinctoria*, Also Known as Folium', *Science Advances* 6, no. 16 (April 2020).

purple, there is still a lot that is unknown about the substances used and methods undertaken to produce these colours. The paper from Lisbon University is critically discussed alongside works by Mario Aceto (mentioned below) in Chapter Four.

Further recent publications, first presented as posters at the Fitzwilliam 'Colour' conference mentioned above, such as *Microspectrofluorimetry and chemometrics for the identification of medieval lake pigments* and *Silver paints in medieval manuscripts: a first molecular survey into their degradation* are technical in approach.[36] Others feature applied technology, such as *The book on how to make all the colour paints for illuminating books: unravelling a Portuguese Hebrew illuminators' manual* and *On the use of EDXRF, mapping-EDXRF and UV-Vis FORS to unveil the step by step production of two illuminated manuscripts from the fifteenth century Portuguese Royal Court*.[37] The latter paper echoes the sentiment of the EDXRF paper published by MINIARE, mentioned above, which suggests that XRF should be combined with other techniques for accurate analysis. This notion is discussed further in Chapter Three.

Mark Clarke

Mark Clarke, a technical art historian at Lisbon NOVA University, has written numerous books and papers on the medieval recipe treatise and technical art-craft works, focusing on colour and pigment production.[38] One of his most recent works, a translation and interpretation of *The Montpellier Liber diversarum arcium,* focuses on recipes and pigment production and is discussed further in Chapter Two.[39]

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[36] Paula Nabais et al., 'Microspectrofluorimetry and Chemometrics for the Identification of Medieval Lake Pigments', *Heritage Science* 6, no. 1 (1 December 2018): 13; Rita Araújo et al., 'Silver Paints in Medieval Manuscripts: A First Molecular Survey into Their Degradation', *Heritage Science* 6, no. 1 (1 December 2018): 8.

[37] Maria J. Melo et al., 'The Book on How to Make All the Colour Paints for Illuminating Books: Unravelling a Portuguese Hebrew Illuminators' Manual', *Heritage Science* 6, no. 1 (1 December 2018): 44; Catarina Alexandra Martins Fernandes Barreira et al., 'On the Use of EDXRF, Mapping-EDXRF and UV-Vis FORS to Unveil the Step by Step Production of Two Illuminated Manuscripts from the Fifteenth Century Portuguese Royal Court', *Microchemical Journal* 153 (2020): 1–9.

[38] Mark Clarke, *The Art of All Colours: Medieval Recipe Books for Painters and Illuminators* (London: Archetype, 2001); FCT/UNL, 'Mark Clarke', accessed 21 December 2020, https://www.dcr.fct.unl.pt/pessoas/professor-auxiliar-convidado/mark-clarke.

[39] Mark Clarke, *Mediaeval Painters' Materials and Techniques: The Montpellier Liber Diversarum Arcium* (London: Archetype, 2011).

At the 'Colour' conference, Clarke presented a paper entitled *Recipes and Reception: Late Medieval English Colour Recipes and Amateur Illuminators*, which reports on the 'very large' corpus of surviving Middle English colour recipes.[40]

ISAAC

At Nottingham Trent University is the Imaging and Sensing for Archaeology, Art History and Conservation (ISAAC) research group, led by a physicist, Haida Laing. Established in 2006, the group's research focuses on developing remote sensing and imaging equipment for work on cultural artefacts, including laser induced spectroscopy from distances of tens of metres.

Recent publications from the group include a paper entitled *From remote sensing and machine learning to the history of the Silk Road: large scale material identification on wall paintings*, which uses an interdisciplinary approach to reveal Sanskrit writings and other evidence to all cave temple paintings to be dated to within a century.[41] Another recent paper details how optical coherence tomography was used to analyse Egyptian faience.[42] A further recent publication co-authored by Liang is an overview of six scientists working in different fields within the arena cultural heritage and describes their work, achievements and discusses how physics and cultural heritage can be intertwined.[43]

Trinity College Dublin

In 2016 Trinity College Dublin (TCD) was awarded funding to analyse, conserve and digitise four early Irish Gospel books – the Codex Usserianus Primus, the Book of Mulling, the Book of Dimma, and the Garland of Howth. These books, together with the Book of Kells, the Book of Durrow, and the Book of Armagh, form a pre-eminent corpus of early Christian medieval art held at the TCD library. Results from the XRF and Raman spectroscopic analysis of the four books formed the basis of Dr Rachel Moss

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[40] Mark Clarke, 'Recipes and Reception: Late Medieval English Colour Recipes and Amateur Illuminators', in *Manuscripts in the Making: Art and Science*, vol. two (London and Turnhout: Harvey Miller/Brepols, 2017).

[41] Sotiria Kogou et al., 'From Remote Sensing and Machine Learning to the History of the Silk Road: Large Scale Material Identification on Wall Paintings', *Scientific Reports* 10, no. 1 (December 2020): 19312.

[42] Margaret Read et al., 'A Non-Invasive Investigation of Egyptian Faience Using Long Wavelength Optical Coherence Tomography (OCT) at 2 Mm', *Studies in Conservation*, 26 February 2021, 1–8.

[43] Marco Leona et al., 'From Physics to Art and Back', *Nature Reviews Physics* 3, no. 10 (October 2021): 681–84.

and Susie Bioletti's paper given at the 'Colour' conference in 2016, which was subsequently published in the conference proceedings.[44]

National Gallery

The National Gallery Technical Bulletin, first published in 1977, is released annually and is thus on its 36th volume. It is a leading publication, spearheaded by Dr Ashok Roy, reporting on the analysis of painting techniques and their scientific examination.[45] Dr Roy has published numerous works on related subjects and collaborated along with others on three volumes - *Artists Pigments* - which have been utilised in this study.[46]

Team Pigment

Based at the University of Durham, Team Pigment is a group of chemists, conservation scientists and historians who analyse pigments using a variety of methods, which are examined in detail in Chapter Three. They are particularly noted for their portable yet sophisticated Raman spectrometer, which at present is the only one customised for work on cultural artefacts in the UK.

Recent publications from Team Pigment include a chapter in the conference proceedings of the Colour Conference at Cambridge University mentioned above.[47] In their study, Team Pigment examined twenty-seven manuscripts thought to have been made in Canterbury. The manuscripts examined, dating from the early tenth century to the late twelfth century, afford a diachronistic study of pigment usage in Southern England in the high Middle Ages. The chapter also reports on the findings of the unexpected pigment Egyptian blue, which was mixed in with lapis lazuli in some manuscripts. This phenomenon is discussed further in Chapter Two.

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[44] Rachel Moss and Susan Bioletti, 'The Art and the Pigments: A Study of Four Insular Gospel Books in the Library of Trinity College Dublin', in *Manuscripts in the Making: Volume One* (Harvey Miller, 2017), 12–20.

[45]National Gallery, 'Technical Bulletin Volume 36', accessed 28 May 2021, https://www.nationalgallery.org.uk/research/research-resources/technical-bulletin/technical-bulletin-volume-36.

[46] Robert L. Feller, ed., *Artists' Pigments: A Handbook of Their History and Characteristics.*, vol. 1 (New York: Oxford Univ. Press, 1986); Ashok Roy and National Gallery of Art, eds., *Artists' Pigments: A Handbook of Their History and Characteristics*, vol. 2 (Washington, DC: National Gallery of Art, 2012); Elisabeth West FitzHugh, *Artists' Pigments: A Handbook of Their History and Characteristics*, vol. 3 (Washington: National Gallery of Art, 2012).

[47] Richard Gameson, Andrew Beeby, and Catherine Nicholson, 'Colour at Canterbury', in *Manuscripts in the Making: Art and Science*, vol. 1 (Harvey Miller Publishers, 2018).

Andrew Beeby has recently published a further book chapter with a member of the Durham University Archaeology department - Dr Kamal Badreshany. This work identifies pigments on artefacts from the Roman settlement Cataractonium (now Catterick, North Yorkshire) and is part of the monograph *Contact, Concord and Conquest: Britons and Romans at Scotch Corner*.[48]

A recently published technical paper is *There's More to Reflectance Spectroscopy Than Lux*, which details a novel system for the examination of manuscripts by UV-NIR FORS, and the associated management of risk when light is shone onto a manuscript.[49] In Chapter Two, this system is explained more fully.

A further technical paper released in 2018 was a library-style paper collating data from sixteen pigments under five different wavelengths of Raman spectroscopic investigation. This paper is mentioned in the notes above. [50]

Aside from technical and wider-ranging studies, Team Pigment has also conducted smaller-scale case studies, where pigment analysis is combined with art-historical examination to provide a detailed investigation into individual volumes, workshops or hands. One such paper that has been published is *The Colour of The Law*, a study on a series of Italian law books made in Bologna in the late thirteenth century. Here, artistic practices between hands can be uncovered and compared – some hands using verdigris for the green in the illuminations, for example, whilst others deploy a mixture of blue and yellow pigments to form vergaut, and others shy away from using green at all.[51]

A similar art-historic meets scientific approach, employed in *The Colour of The Law* above was used in *The Admiral, the Virgin, and the Spectrometer: Observations on the Coëtivy Hours (Dublin, Chester Beatty Library, MS W082),* which was published in Gesta in 2020 by Team Pigment. [52] This paper

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[48] Andrew Beeby and Kamal Badreshany, 'Pigment Analysis', in *Contact, Concord and Conquest: Britons and Romans at Scotch Corner* (Archaeology Data Service, 2021), https://archaeologydataservice.ac.uk/archives/view/scotch_a1_2021/, pp. 23-28.

[49] Andrew Beeby et al., 'There's More to Reflectance Spectroscopy than Lux', *Journal of the Institute of Conservation*, 8 May 2018, 1–12. Please note that L. Garner is a co-author on this paper.

[50] G. Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', *Analytical Methods* 10, no. 10 (2018).

[51] Richard Gameson et al., 'The Colour of the Law', *Codices Manuscripti et Impressi*, no. 112/113 (2019).

[52] Richard Gameson, Catherine Nicholson, and Andrew Beeby, 'The Admiral, the Virgin, and the Spectrometer: Observations on the Coëtivy Hours (Dublin, Chester Beatty Library, MS W082)', *Gesta*, 14 October 2020, pp. 203 - 231.

examines the Marian texts and imagery in the mid-fifteenth-century Parisian Coëtivy Hours, as well as reporting the findings from the scientific investigation of the inks and pigments that were deployed.

Forthcoming is a paper *Late Medieval English Illuminators Blues*.[53] This paper discusses the different blue pigments deployed in English manuscripts in the fifteenth century. Their relative costs, ease of procurement, and nature of employment uncover the complex and intertwined circumstances that pigment choice reveals.

The Pigments of British Illuminators: A Scientific and Cultural Investigation

In 2018, the Arts' and Humanities Research Council (AHRC) provided approximately half a million pounds to a joint venture by Team Pigment and MINIARE to fund three years of further research into the pigments used in the British Isles between the fifth and the fifteenth century. (Due to the impact of the pandemic, the study has been extended.) By the end of the study, over two hundred manuscripts made in various production centres around Britain across the period will have been analysed. This research will form the basis of the publication of a handbook that will be the first scientific account of the pigments of British illuminated manuscripts, and as such, will be a seminal work for future research in the field.

Post-1997 - Notable individuals

As well as teams of scholars and group projects, there are also several individuals whose work it would be remiss not to include in an overview of the field.

David Howell

Formerly Head of Heritage Science within the special collections department at the Bodleian Library, Oxford, David Howell has worked closely with the Ashmolean Museum and Team Pigment to analyse artefacts in the Bodleian's collection, and elsewhere. In 2020 Howell published a book with co-author Ludo Snijders - *Conservation Research in Libraries.*[54]

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[53] Richard Gameson et al., 'Late Medieval English Illuminators' Blues', (forthcoming). Please note that L. Garner is named on this paper.

[54] David Howell et al., *Conservation Research in Libraries*, Current Topics in Library and Information Practice (Berlin: De Gruyter Saur, 2020).

Robin Clark

Robin Clark, now deceased, is credited with producing the first library of Raman Spectra of medieval pigments and binders, published in 1997.[55] This library of data is occasionally referred to in this study.

Cheryl Porter

Cheryl Porter is Director of the Montefiascone Project and Consultant to the Conservation Department at the Library of Alexandria in Egypt. The Montefiascone Project runs a summer school in Book conservation. Porter presented a paper at the Cambridge 'Colour' conference in 2016 on metals in decorations of Cambridge manuscripts. In addition, Porter has also worked closely with Aceto (below) on the identification of purples - a notoriously tricky colour to determine.

Maurizio Aceto

From Universita Del Piemonte Orientale, Maurizio Aceto has published dozens of papers on the identification of pigments. His latest published work is on using DRIFT (Diffuse Reflectance Infrared Fourier Transform) to analyse pigments in situ.[56] He is well-known for his work on the identification of purple colourants. [57] Many of his papers are discussed in detail in this study, including one published with Cheryl Porter, above, Looking *for Lichen, Fooled by Folium and Tricked by Tyrian: a Brief Tour and New Research on Purple in Manuscripts* which was presented at the 'Colour' conference and which is discussed in Chapter Four of this study.[58]

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[55] I. M. Bell, R. J. Clark, and P. J. Gibbs, 'Raman Spectroscopic Library of Natural and Synthetic Pigments (Pre-Approximately 1850 AD)', *Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy* 53A, no. 12 (15 October 1997): 2159–79.

[56] Marcello Manfredi et al., 'Non-Invasive Characterization of Colorants by Portable Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy and Chemometrics', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 181 (June 2017): 171–79

[57] Cheryl Porter et al., 'Looking for Lichen, Fooled by Folium and Tricked by Tyrian: A Brief Tour and New Research on Purple in Manuscripts', in *Manuscripts in the Making: Volume Two* (Harvey Miller, 2017).

[58] Porter et al., 'Looking for Lichen, Fooled by Folium and Tricked by Tyrian: A Brief Tour and New Research on Purple in Manuscripts'.

Peter Vandebeele

From Ghent University, Peter Vandebeele has published many papers on related topics and has most recently published an article measuring the degradation and discolouration of medieval pigments.[59]

Nancy Turner

Nancy Turner is a specialist manuscript conservator at The Getty Museum in California, USA. A recent publication of hers has focused on the materiality of parchment, whilst her latest paper examines a binding in the Getty Collection.[60] In the Cambridge 'Colour' conference, one of Turner's paper focused on the use of XRF to discern more about the use of gold and other metals in Renaissance manuscripts.[61] Another paper, co-authored with Catherine Schmidt Patterson, used XRF, FORS and Raman spectroscopy to analyse eight Byzantine, Armenian and Sicilian manuscripts dating from c. 1100 to c.1300.[62] The findings – the use of smalt, arsenic sulfide glass, lead-tin yellow type I and II, arsenic sulfide glass, amongst other pigments – indicate that these substances were employed in some areas of Europe well before they became known as standard pigments within Northern Europe. [63]

Lucia Burgio

London's Victoria and Albert Museum's Senior Scientist is Dr Lucia Burgio, who has worked in research at the Museum for over twenty years. Her doctorate was supervised by Robin Clark, mentioned above.

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[59] Alessia Coccato, Luc Moens, and Peter Vandenabeele, 'On the Stability of Mediaeval Inorganic Pigments: A Literature Review of the Effect of Climate, Material Selection, Biological Activity, Analysis and Conservation Treatments', *Heritage Science* 5, no. 1 (December 2017)

[60] Nancy K. Turner, 'The Materiality of Medieval Parchment: A Response to "The Animal Turn"', *Revista Hispánica Moderna* 71, no. 1 (2018): 39–67; Nancy K. Turner, 'A Romanesque Binding in The J. Paul Getty Museum: Materials, Craft Technology, and Monastic Reform', *Journal of Paper Conservation: Special Issue in Memory of Christopher Clarkson* 20 (2020): 1–20.

[61] Nancy K. Turner, 'Reflecting a Heavenly Light: Gold and Other Metals in Medieval and Renaissance Manuscript Illumination', in *Manuscripts in the Making: Volume Two* (Harvey Miller, 2017), 81–96.

[62] Nancy K. Turner and Catherine M. Schmidt Patterson, 'New Discoveries in the Painting Materials in the Medieval Mediterranean: Connections between Manuscript Illumination and Glass Technology during the Byzantine Era, c.1100-1300', in *Manuscripts in the Making: Art and Science*, vol. One (London and Turnhout: Harvey Miller/Brepols, 2017), p. 185.

[63] Turner and Schmidt Patterson, 'New Discoveries in the Painting Materials in the Medieval Mediterranean: Connections between Manuscript Illumination and Glass Technology during the Byzantine Era, c.1100-1300', p. 190.

She has been an Honorary Research Fellow at University College London since 2001 and has also chaired the AMC Heritage Science sub-committee, Royal Society of Chemistry, since 2014.

Burgio's most recent publication is *Pigments, Dyes and Inks: Their Analysis on Manuscripts, Scrolls and Papyri* which, as its name suggests, is an overview of the interdisciplinary field of the scientific analysis of written cultural articles and wall-paintings. [64] A protocol for examination of artifacts is discussed, as well as information on which analysis befits which artefact and when, with the invasiveness and destructiveness of each procedure considered.

Another recent publication is a study that combines scientific techniques (FORS) with data analysis, alongside connoisseurship approaches, in order to establish a production chronology for 141 woodblock prints of Katsushika's Hokusai's Thirty-Six Views of Mount Fuji series. The study was able to discern early nineteenth-century prints from early twentieth-century prints and distinguish between different clusters of production.[65]

Also published recently in a paper that focuses on the use of arsenic sulfide glass, a synthetic form of orpiment, in early eighteenth-century London woven silk production. The arsenic sulfide glass was detected by XRF and Raman spectroscopy (techniques that are described in Chapter Three).[66] As explained in Chapter Two, the orange-yellow pigment arsenic sulfide glass is so-called because of its chemical composition; it is not a glass in the common sense of the word.

A further publication of interest to this study is a paper published in 2018 documenting the (then) first intentional use of calomel (mercury I chloride) on a seventeenth-century Peruvian table cabinet.[67] Calomel can be a degradation product of cinnabar, and, as mentioned above, Ricciardi has subsequently found an earlier use of the substance intentionally in a manuscript.

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[64] Lucia Burgio, 'Pigments, Dyes and Inks: Their Analysis on Manuscripts, Scrolls and Papyri', *Archaeological and Anthropological Sciences* 13, no. 11 (November 2021): 194.

[65] Marc Vermeulen et al., 'Beyond the Connoisseurship Approach: Creating a Chronology in Hokusai Prints Using Non-Invasive Techniques and Multivariate Data Analysis', *Heritage Science* 8 (26 June 2020), p. 1.

[66] Lucia Burgio et al., 'Orange for Gold? Arsenic Sulfide Glass on the V&A Leman Album', *Journal of Raman Spectroscopy* 50 (23 June 2019), p. 1169.

[67] Lucia Burgio et al., 'Identification, Characterisation and Mapping of Calomel as "Mercury White", a Previously Undocumented Pigment from South America, and Its Use on a Barniz de Pasto Cabinet at the Victoria and Albert Museum', *Microchemical Journal* 143 (1 December 2018), p. 220.

A forthcoming work that is awaiting publication in the journal Archaeological and Anthropological Sciences, as part of a special edition, is *Pigments - As-based yellows and reds,* with Elisabetta Gliozzo as a co-author.

Robert Fuchs

Robert Fuchs is Head of Restoration and Conservation of Archivals, Books and Manuscripts at the Cologne Institute of Conservation Sciences. One of his papers at the 'Colour' conference concentrated on the analysis of metals in illuminated manuscripts.[68] In another paper, co-authored with Dr Doris Oltrogge, painting techniques and workshop practices in early fourteenth-century Zurich were examined.[69] Although the time and place of this study are not overly relevant to this work, the techniques utilised in the study (XRF and the capturing of under-drawings by infrared imaging) are comparable, and the tentative identification of brazilwood (detailed more in Chapter Two and tentatively identified in this study in Chapter Four) are worthy of note.

Patricia Lovett

Lovett's approach to manuscript studies is through recreation and art - she is a professional artist and calligrapher. Her modern approach to artwork can help inform past practice, and videos of her work on how to make medieval manuscripts were featured in the British Library's Anglo-Saxon Kingdoms exhibition.[70]

John K. Delaney

As well as publishing with Paola Ricciardi from MINIARE (as mentioned above), John Delaney, an imaging scientist at the National Gallery in Washington, has also published a recent study with colleagues. The paper, published in the 'Colour' conference proceedings, reports findings from hyperspectral diffuse reflectance imaging spectroscopy (RIS) alongside FORS and XRF, on two

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[68] Robert Fuchs, 'Gold or Brass, Silver or Tin: The Analysis of Metals in Medieval Book Illumination', in *Manuscripts in the Making: Volume Two* (Harvey Miller, 2017), 97–106.

[69] Doris Oltrogge and Robert Fuchs, 'The Vadiana Rudolf of Ems: Painting Techniques in Fourteenth-Century English Manuscripts', in *Manuscripts in the Making: Art and Science*, vol. one (London and Turnhout: Harvey Miller/Brepols, 2017), pp. 65-74.

[70] British Library Website, 'How to Make a Medieval Manuscript' (The British Library), accessed 16 July 2020, https://www.bl.uk/medieval-english-french-manuscripts/articles/how-to-make-a-medieval-manuscript.

illuminations attributed to the Master of the Dominican Effigies. These results were then analysed and combined to produce false-colour image maps of pigment position and identification.[71]

Miscellaneous

Lapis lazuli in the dental calculus of a female religious woman

Published in 2019, the paper *Medieval women's early involvement in manuscript production suggested by lapis lazuli identification in dental calculus* somewhat caught the public imagination as it reaffirmed, and brought into centre stage, the notion of female scribes.[72] The paper reports that the dental calculus of a late-eleventh or early twelfth-century religious female in Germany was examined and found to contain lapis lazuli, inferring from its presence that she was either a scribe or a paint-maker in a scriptorium and had ingested the blue pigment either by licking her paintbrush when painting or by inhalation of the blue powder when, for example, grinding the pigment. Undoubtedly, the presence of the material confirms that lapis lazuli was available in Germany at that time. Although lapidary medical ingestion and devotional osculation have been considered and discounted in the paper, and the paper's opinion sways heavily towards the woman having been a scribe or preparing pigment in some way, it seems unlikely, based on the evidence of lapis lazuli in the dental calculus alone, that the truth will emerge.

Sarah Fiddyment

Formerly at York University and now at Cambridge University, Sarah Fiddyment specialises in the non-invasive analysis of DNA from parchment. Biocodicology, the study of biological information stored in manuscripts, can reveal knowledge about book production, livestock economies, and historic use. Fiddyment's latest publication, published with Matthew Teasdale, Matthew J Collins and Jiří Vnouček, amongst others, is a field guide to the subject.[73]

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[71] John K. Delaney et al., 'Mapping and Identification of the Pigments Used in Two Illuminations from the Laudario of Sant'Agnese Attributed to the Master of the Dominican Effigies', in *Manuscripts in the Making: Art and Science*, vol. two (London and Turnhout: Harvey Miller/Brepols, 2017), pp. 156-168.

[72] A. Radini et al., 'Medieval Women's Early Involvement in Manuscript Production Suggested by Lapis Lazuli Identification in Dental Calculus', *Science Advances* 5, no. 1 (January 2019).

[73] Sarah Fiddyment et al., 'So You Want to Do Biocodicology? A Field Guide to the Biological Analysis of Parchment', *Heritage Science* 7, no. 1 (2019): 35.

Jiří Vnouček

Jiří Vnouček is based at both York University, where there is a collaboration between the Biology, Archaeology and Chemistry departments (BioArCh) and The Royal Library, Copenhagen, where he is a conservator. He employs visual methods to assess and discern parchment types, which in turn can inform on the place, dating and methods of manuscript production, as well as provide information that may help to identify groups of similar manuscripts. He has worked with Fiddyment (mentioned below) on the analysis of parchment by DNA, and a paper published by Vnouček, Fiddyment and others on uterine vellum, which is very relevant to this study, is discussed in Chapter Four. [74]

Scholarship in the field of Paris bibles and thirteenth-century manuscript material culture

The Paris Bible genre is discussed in detail in Chapter Four of this thesis, where the identifying features of the text type are examined, alongside a brief history of how and why the phenomenon of 'The Paris Bible' emerged. In Chapter Two, manuscript manufacture in thirteenth-century Paris is discussed. This section, therefore, aims to provide an overview of the scholarship relating to these two areas, with an additional focus on work that has been conducted on pigment analysis. As briefly mentioned above, unlike scientific research, the study of manuscript culture remains 'current' for longer. Whilst, of course, new scholarship emerges periodically, it is usually built upon the foundations of seminal work that has gone before, rather than focusing on the novel or previously unexamined, as is the case in most scientific scholarship. This section focuses on these formative works, as well as the foremost recent research.

The chronology of scholarship that surrounds Paris Bibles begins in the nineteenth and twentieth century, when individual manuscripts were classified in detail by cataloguers at their repositories, meaning that connections between manuscripts, their palaeography, and codicology could be made more easily. Montague Rhode James, a leading English scholar of the early twentieth century, was one such scholar, for example.[75] Of course, that is not to suggest that manuscripts had never been 'catalogued' before the nineteenth century – lists of books in libraries date back to antiquity. However, the more modern 'descriptive catalogues' from this period allowed for links and relationships to be made more easily, and details to be mined.

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[74] Sarah Fiddyment et al., 'Animal Origin of 13th-Century Uterine Vellum Revealed Using Noninvasive Peptide Fingerprinting', *Proceedings of the National Academy of Sciences* 112, no. 49 (8 December 2015).

[75] Ralph Hanna, 'Manuscript Catalogues and Book History', *The Library* 18, no. 1 (March 2017), p. 47.

Certainly, someone who extracted information from these catalogues was Jean Porcher (d. 1966) who, in his role as *conservateur en Chef* of the manuscripts department at the Bibliothèque Nationale in Paris convened two exhibitions on French illuminated medieval manuscripts, in 1954 and 1955. The second of these focussed on manuscripts of the thirteenth, fourteenth and fifteenth centuries.[76] A review of the second showcase described it as "an unforgettable spectacle" and pronounced the exposition and catalogues as "major events in the history of the study of medieval.... manuscripts."[77] The shows later resulted in Porcher producing a survey of French manuscript painting that was published in 1959. In addition to this work, he also photographed many of the manuscripts in the collection and published many facsimile copies.

Moving from general French manuscript illumination of the medieval period, to the to the specific, was Robert Branner's seminal work *Manuscript Painting in Paris during the Reign of Saint Louis: A Study of Styles*, published in 1977. This work provides crucial background information regarding what is known of the ateliers in Paris in the thirteenth century, their location, and house style.[78] The book provides a comprehensive survey of artwork and attempts to classify artwork by atelier. Although survey work on Paris Bibles has been repeated and has refined aspects of Branner's work (Chiara Ruzzier's comparative study *The Miniaturisation of Bible Manuscripts in the Thirteenth Century*, for example) Branner's work still remains the starting point of such analysis, and thus, its work is central to this thesis.[79]

De Hamel's works similarly provide a cultural context for thirteenth-century Paris, particularly his 1994 work in *A History of Illuminated Manuscripts*.[80]

Following these works was Rouse and Rouse's two-volume publication of manuscript manufacture and trade in Paris from 1200-1500.[81] First published in 2000 and republished as a special edition in

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[76] Art Historians Website. 'Porcher, Jean', accessed 31 July 2021, https://arthistorians.info/porcherj.

[77] Millard Meiss, 'The Exhibition of French Manuscripts of the XIII-XVI Centuries at the Bibliotheque Nationale', *The Art Bulletin* 38, no. 3 (September 1956): 187, p. 188.

[78] Robert Branner, *Manuscript Painting in Paris during the Reign of Saint Louis: A Study of Styles*, California Studies in the History of Art 18 (Berkeley: University of California Press, 1977).

[79] Chiara Ruzzier, *The Miniaturisation of Bible Manuscripts in the Thirteenth Century. A Comparative Study*, *Form and Function in the Late Medieval Bible* (Brill, 2013).

[80] Christopher De Hamel, ed., *A History of Illuminated Manuscripts*, 2. ed. (London: Phaidon Press, 1994).

[81] Richard H. Rouse et al., eds., *Medieval Manuscripts, Their Makers and Users: A Special Issue of Viator in Honor of Richard and Mary Rouse* (Turnhout, Belgium: Brepols, 2011).

2011, it is widely regarded as a landmark study (one review calls it 'magisterial') and is a germane resource for examining book making in the thirteenth century.[82]

Further works on manuscript illumination of the period include Stahl's *Picturing Kingship,* published in 2008, which presents an art-historical investigation on St. Louis' personal prayer book.[83] In addition, there is Jackson, Morgan and Panayotova's 2009 work on Illumination in France 1000-1250, whose study overlaps with the period of analysis in this research.[84]

The genre and identification of Paris Bibles have since been the source of much exploration. Eyal Poleg and Laura Light's publication *Form and Function in the Late Medieval Bible* is a collection of papers originally presented at Edinburgh University in July 2010 and is an important recent publication utilised in this study.[85] The focus, as the title suggests, is on late medieval bibles, and although not all the papers contained concentrate on artwork, the study does encompass scholarship that is pertinent to this work, including Richard Gameson's chapter *Durham's Paris Bible and the Use of Communal Bibles in a Benedictine Cathedral Priory in the Later Middle Ages*. Other work published by (for example) Murano continues to examine the archetypal Paris Bible's actual text in detail.[86]

With art history and text type well documented, it becomes clear that, up until very recently, there has been an omission in the available literature to address the scientific analysis of these works. In 2007, Inès Villela-Petit published *'Palettes comparées: quelques réflexions sur les pigments employés par les enlumineurs parisiens au début du XVe siècle'* which is a study of the pigments in ten Parisian manuscripts dating from c. 1400.[87] Although the Villela-Petit study is a very useful peripheral work, it

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[82] 'Illiterati et Uxorati. Manuscripts and Their Makers: Commercial Book Producers in Medieval Paris 1200-1500', accessed 31 July 2021, https://hnanews.org/hnar/reviews/illiterati-et-uxorati-manuscripts-makers-commercial-book-producers-medieval-paris-1200-1500/.

[83] Harvey Stahl, *Picturing Kingship: History and Painting in the Psalter of Saint Louis* (University Park, Pa: Pennsylvania State University Press, 2008).

[84] Nigel J. Morgan, Stella Panayotova, and Martine Meuwese, eds., *Illuminated Manuscripts in Cambridge: A Catalogue of Western Book Illumination in the Fitzwilliam Museum and the Cambridge Colleges* (London: Harvey Miller, 2009).

[85] Eyal Poleg and Laura Light, eds., *Form and Function in the Late Medieval Bible*, Library of the Written Word, Vol. 27 (Leiden ; Boston: Brill, 2013).

[86] Giovanna Murano, 'Chi Ha Scritto Le Interpretationes Hebraicorum Nominum?', in *Étienne Langton, Prédicateur, Bibliste, Théologien*, vol. 9, Bibliothèque d'histoire Culturelle Du Moyen Age 9 (Brepols Publishers, 2010), 353–71.

[87] Inès Villela-Petit, 'Palettes Comparées: Quelques Réflexions Sur Les Pigments Employés Par Les Enlumineurs Parisiens Au Début Du XV ^{e} Siècle', in *Quand La Peinture Était Dans Les Livres*, ed. Mara Hofmann, Eberhard König, and Caroline Zöhl, vol. 15 (Turnhout: Brepols Publishers, 2007), 383–92.

is evident that there has been little scientific analysis of any sort on thirteenth-century Paris bibles. This omission is likely to be because the zenith of Parisian manuscript painting is widely considered to be between 1380 – 1425 when artists such as the Boucicault Master and the Master of the Mazarine Hours were pioneering new ways of representation on the page.[88] Furthermore, in the later fifteenth century, the artist Jean Fouquet brought Italian Renaissance techniques into French painting. With fantastic full-page artworks such as those from *The Hours of Etienne Chevalier* (Bl. Additional 16997) making a more obvious starting point for pigment and other scientific analysis, this has meant that other earlier Parisian and northern European manuscripts have perhaps been overlooked.

In 2021 Panayotova et al. published a work that goes some way to redressing this lacuna, with short case studies of scientific analysis of several Parisian ecclesiastical texts from the thirteenth century, as well as some southern English manuscripts of the same period, although this work stops short of analysing any thirteenth-century Paris bibles.[89] Therefore with a secure amount of scholarship on the artwork and text type of Paris bibles and some small scale investigation into similar works, this thesis seeks to build upon this foundation to add to the weight of scholarship in this area, redress the omission of scientific analysis of thirteenth-century Paris bibles, and provide further information so that knowledge of these splendid, but slightly overlooked, books can be increased.

[88] C. Wight, 'The British Library Catalogue of Illuminated Manuscripts', Text (The British Library), accessed 27 May 2021, https://www.bl.uk/catalogues/illuminatedmanuscripts/TourFrIntro.asp#HIST.

[89] Panayotova, *Scientific Analysis of Illuminated Manuscripts*.

Chapter Two

Manuscript Production

Colours: Recipes, Dyes and Pigments

Manuscript Production

Context

This chapter is in two sections. The first section examines briefly how manuscripts are made and the main components in their creation. An overview of the distinctive circumstances in which manuscripts were produced in Paris in the thirteenth century is presented, as this 'sets the scene' for six of the seven manuscripts analysed later in this study. The second section details the pigments and dyes employed to colour the artwork in manuscripts of this period. An overview of the pertinent chemistry and known trade routes for each pigment is provided, giving a context for their inclusion in a manuscript.

What is a manuscript?

The word manuscript derives from the Latin words for 'by hand' (*manu*) and 'written' (*scriptus*) and so a manuscript is technically anything written by hand. This definition is so broad as to include hastily jotted shopping lists as well as hand-carved Roman inscriptions. In practice the term *codex* (latterly taken to mean a book constructed from paper, parchment, or papyrus) is employed. A manuscript in this sense differs from an early printed book (an incunabulum).

The codex as the principal form of literary text took over from *rotuli,* rolls of papyrus, in the fourth century. In Northern Europe, this change was probably hastened due to the climate; there would have been a plentiful supply of good quality parchment with British weather, in particular, providing lush

grass for cattle, but papyrus would need to have been imported from papyrus growing regions, ostensibly the Nile.[1] However, the exact circumstances for the switch remain a matter of debate.[2]

Manuscript production in Paris

From the seventh century until the end of the twelfth century, manuscript manufacture was mostly completed in ecclesiastical settings. These institutions, and in particular their scriptoria, were the powerhouses that produced and disseminated manuscripts. Most books were copied for use 'in house' or for other ecclesiastical communities. There is increasing evidence for lay participation in book production during the course of the twelfth century, and by the thirteenth century lay workers in urban centres had become the principal producers.[3]

De Hamel describes the flourishing university education system of Paris in the twelfth century as central to the growing book trade.[4] Certainly, there is evidence that by the thirteenth century second-hand secular and religious books were being traded in Paris – a far cry from the ecclesiastical monopoly that had previously endured. However, despite evidence for trade in previously-owned manuscripts, from before the thirteenth century, there is scant evidence of large scale secular production until after the Bible was redesigned from large and unwieldy to small and portable, even pocket-sized. A section on how and why this change occurred can be found in Chapter Four.[5]

By the mid-thirteenth century, secular book production in Paris (of both secular and ecclesiastic manuscripts) had almost taken over from ecclesiastical production. The city was replete with booksellers, parchmenters, scribes, pen flourishers, and illuminators. Furthermore, Paris was becoming a 'hub', famous for its manuscript production - drawing itinerant illuminators and scribes from across Europe. Illuminators often worked in ateliers, each with a distinctive house style. [6] With a great many artisans at work, a vast number of manuscripts were produced at speed - helped, no doubt,

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[1] Richard Gameson et al., eds., *The Cambridge History of the Book in Britain* (Cambridge, UK ; New York: Cambridge University Press, 1998), p. 2.

[2] Colin H. Roberts and Theodore C. Skeat, *The Birth of the Codex* (London: Oxford Univ. Press, 1987); Francis Watson, 'The Canon and the Codex: On the Material Form of the Christian Bible', in *The Life of Texts: Evidence in Textual Production, Transmission, and Reception* (London: Bloomsbury Academic, 2019), pp. 48-61.

[3] Richard H. Rouse et al., eds., *Medieval Manuscripts, Their Makers and Users: A Special Issue of Viator in Honor of Richard and Mary Rouse* (Turnhout, Belgium: Brepols, 2011); C. Wight, 'The British Library Catalogue of Illuminated Manuscripts', Text (The British Library), accessed 21 December 2020, https://www.bl.uk/catalogues/illuminatedmanuscripts/TourFrIntro.asp.

[4] Christopher De Hamel, ed., *A History of Illuminated Manuscripts*, 2. ed. (London: Phaidon Press, 1994), p. 113.

[5] De Hamel, p. 124.

[6] Robert Branner, *Manuscript Painting in Paris during the Reign of Saint Louis: A Study of Styles*, California Studies in the History of Art 18 (Berkeley: University of California Press, 1977), p. 21.

by the formation of the *pecia* system, described below. By 1300 the book trade in Paris was very well established and under university control, and in 1316 booksellers were required to take an oath to uphold trade and copying regulations.[7]

The *Pecia* System

Although many questions remain about the precise nature of the *pecia* system, in essence, the arrangement allowed the process of manuscript production to be expedited by disassembling (or perhaps never assembling) a manuscript into 'pieces' (from the word *pecia*), numbering them, and then lending out each section, in order that several scribes could be copying several sections of a manuscript at once. Therefore, a scribe could be one of several making a full copy of a text, or be one of many contributing to making one copy of a text. In turn, the reproduced section could then itself be copied, and there were arrangements in place to allow these reproductions to be checked against the original. In theory, copies were therefore only ever one step away from the original.[8]

Durham Cathedral holds the earliest datable manuscript related to the *pecia* system (MS A.I.16), which is a copy of Hugh of St. Cher on the Pauline Epistles.[9] *Pecia* numbers (a way for the scribe, his employers, and the bookseller hiring the *pecia*, to easily see which *pecia* has been copied) are found marking the manuscript, which was bequeathed to Durham Cathedral in 1258, so it is clear that the system was in action before that date.

Writing and decorating manuscripts - the components

Pens, pen-knives, and brushes

Most scribes would have a pen (or quill), made from the hardened and trimmed feather of a large bird - a goose, swan, or crow, for example, as shown in Figure 1.[10] A small notch cut into the pen would have held the ink or pigment, and required regular dipping to refill it. A pen-knife would have been used to trim the quill periodically, as the notch splays during writing. The pen-knife would also have been employed to erase mistakes - the scribe could simply scrape off the ink (and with it a thin layer of the parchment membrane) using the knife.

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[7] De Hamel, *A History of Illuminated Manuscripts*, p. 127.
[8] De Hamel, p. 131.
[9] De Hamel, p. 136.
[10] Fitzwilliam Museum Website. 'Making Art in Manuscripts', accessed 8 May 2017, http://www.fitzmuseum.cam.ac.uk/pharos/sections/making_art/manuscript.html.

Figure 1: Illustration of an inkpot, pen-knife, and quill for writing and parchment page.

Small brushes made from the hair of an animal - usually a squirrel, occasionally a badger or hog - were sometimes used for illumination. However, often the artwork was completed with a similar pen to that employed to write the text.[11]

Paints and palette

Pigments and dyes would have been prepared by the illuminator or by an assistant and made into paint ready for application by pens or brushes. Single pigments, in small quantities to avoid waste, were often kept in a shell ready for painting. In the early and high medieval period, colours tended to be applied separately, with shading executed by layering paint, and other effects created by adding embellishments such as dots and lines to give the impression of a wider range of hues. Occasionally colourants were combined - black was added to darken a colour or white to lighten it, and pinks, browns and some greens were the result of combining two or more colours. A more thorough explanation of the pigments and dyes used in illuminations is detailed in the next section.

Binders

A binder is a material, usually proteinaceous, with which insoluble pigment particles are mixed in order that it may adhere to the writing support. It should not alter the pigment in any way. In medieval manuscripts, various binders were employed, especially gum Arabic (the sap from the acacia tree) and

[11] Gerald W. R. Ward, ed., *The Grove Encyclopedia of Materials and Techniques in Art* (Oxford ; New York, NY: Oxford University Press, 2008), p. 481.

glair (egg white). Additionally, egg yolk, honey, resin, and parchment glue or 'size' (glue made from parchment clippings and/or other animal parts such as horn) have also been detected as binders or glazes. It is possible that other substances, such as different resins and saps, yet to be ascertained, were also used.[12] Medieval treatises often recommended the preferred medium for each pigment. Mrs Merrifield's *Original Treatise* offers many translations of recipes and tips surrounding their use.[13]

Gold and silver illumination

Precious metals were often used to 'illuminate' or capture light in medieval manuscripts. Finely beaten leaf gold or silver was applied either directly to the page or to a mound of gesso. Recipes for gesso vary, but generally a mixture of plaster, a white pigment such as white lead, sugar, glue and a red or brown pigment such as red lead or Armenian bole (added to produce a pink colour thought to enhance the colour of gold) were used. Once applied, the gold was generally burnished with a tooth set into a holder, see Figure 2, and possibly tooled or punched with a decorative stamp.

Figure 2: A burnishing tooth, set in a tool.

Shell gold and silver was also deployed, so called as finely ground metal was made into paint in the shells that held pigments ready for use. This material was more expensive even than gold leaf.[14] Mosaic gold, another gold substitute, is a form of tin (IV) sulfide.[15] The chemistry of the metals, and faux metals, that were deployed in manuscripts are examined in more detail below.

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[12] Stella Panayotova et al., eds., *Colour: The Art & Science of Illuminated Manuscripts* (London Turnhout: Harvey Miller Publishers, 2016), p. 38.

[13] M. P. Merrifield, *Original Treatises: Dating from the XIIth to XVIIIth Centuries on the Arts of Painting, in Oil, Miniature, Mosaic, and on Glass; of Gilding, Dyeing, and the Preparation of Colours and Artificial Gems; Preceded by a General Introduction; with Translations, Prefaces, and Notes* (J. Murray, 1849), p. 156.

[14] Fitzwilliam Museum Website, 'Making Art in Manuscripts'.

[15] Panayotova et al., *Colour*, p. 37.

Colours: Recipes, Pigments and Dyes

Context

This section explores the colourants that were created and deployed in medieval manuscript illumination, with a particular emphasis on those that may have been available in the High Middle Ages, which is when the manuscripts examined later in this thesis were created.

The first section is a discussion of recipe collections, prominent artists, and scholars relating to the processing of pigments and paint making. There then follows an in-depth examination of the pigments and dyes employed. The chemistry and pertinent geology of each colour stuff is briefly discussed, providing a context for its deployment.

Those colourants whose presence in medieval manuscripts is undisputed are examined. Furthermore, those colourstuffs that are regularly described in medieval recipe collections, but whose presence in manuscripts cannot currently be confirmed by non-destructive investigation, are also included; in the future, as technology develops, they may well be identified. A brief description of pertinent modern pigments is also included, as these are occasionally found in manuscripts - in the work of a conservator, or, in rare cases, a forger.

Recipe books

The curation, copying and transmission of medieval pigment recipe treatises is too extensive and nebulous a subject to explore in depth in the present study; it has been suggested that there are at least 450 surviving manuscripts that contain technical details and recipes for artists.[16] Therefore, only a short introduction to prominent texts and scholars of the subject is provided here. The texts and authors below are included either because modern sources refer to them often or because they date from the High Middle Ages and so provide an apposite insight into the art culture at the time that the manuscripts examined in this study were made.

Interestingly, there is a shift in the content of recipe books shortly after the time of the focus of this study. From c.1300 recipe books began to focus on painting technique, such as making mixtures and glazes, and on the preparation of dyes and lakes, rather than on the classification and manufacture of pigments, which had been the content previously.[17] This change is likely the result of pigment

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[16] Mark Clarke, *Mediaeval Painters' Materials and Techniques: The Montpellier Liber Diversarum Arcium* (London: Archetype, 2011), p. 9.
[17] Clarke, p. 12.

preparation having moved from 'home-made' to wholesale. The workshop artist need not have concerned him/herself with the preparation of colourants when they could be easily purchased.

As Mark Clarke mentions in his commentary on The Montpellier *Liber diversarum arcium* below, the manuscript is 'hyper-complete' and could have been severely edited to be more useful. This informs the notion that some of the recipe collections that survive today are likely those that were 'para-literary texts' for interested general readers – actual workshop manuals would probably have been shorter and more practical, and as they were likely heavily used, have not survived to the modern day.[18]

Classical Scholars

Several scholars from antiquity, including Theophrastus (d. 288 BCE), as well as Pliny and Vitruvius from the first century BCE, wrote notes and comments on pigment manufacture. However, it is probably only Vitruvius who had any experience of actually making or working with pigments.[19] Vitruvius was an engineer whose treatise 'On Architecture' contains ten books, the seventh of which addresses interior decoration and wall painting.[20]

Mappae Clavicula

Several manuscripts, dating from the eighth to the twelfth century can be classed as belonging to the Mappae Clavicula tradition. Each tract is a compendium of recipes; the most substantial version of the text (the Lucca Manuscript - BCF Codex 490) contains over 300 recipes and dates from c.800. Many other manuscripts in this family are probably variations on a core text that was compiled by an anonymous author around 600 CE, although later versions of the text do subsume new recipes, particularly Arabic ones, that became known in the twelfth century.

De coloribus et mixtionibus

This tract attributed to 'Heraculus' is sometimes found alongside the Mappae Claviculae and sometimes as a standalone treatise. It originated in northern France or England around 1100 CE.

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[18] Clarke, p. 41.
[19] Clarke, p.10.
[20] Grove Art Online, 'Vitruvius', accessed 17 October 2020, https://www.oxfordartonline.com/groveart/view/10.1093/gao/9781884446054.001.0001/oao-9781884446054-e-7000089908.

Divers arts

Theophilus' *Divers Arts (De diversis artibus)* or *Schedula* as it is sometimes known, dates from around 1100 CE and was produced in north-west Germany. Theophilus is a pen name; the author describes in the work how he does not wish for recognition – he would rather dedicate his talents to God. One later copy of the text attributes the work to a Belgian or German monk named Roger, who was a goldsmith.[21]

The text is in three parts, the first of which deals with wall, panel, and manuscript painting. As well as methods of preparation for pigments and binders, the text delves into painterly techniques such as highlighting and shading. The second book concerns glass-making, and the third book deals with metalworking. The author assures the reader that he has practical experience in the production and testing of his recipes. The work is considered to be one of the foremost accounts of the working methods of artists in the medieval period and is notable on account of its originality – most of the recipes and descriptions are novel and do not appear to be copied from other treatises.[22]

The Montpellier Liber diversarum arcium

The Montpellier *Liber diversarum arcium* (translated as 'Book of Various Arts') is part of MS H277 held at the Bibliotheque interuniversitaire, in Montpellier, France. Thought to date from around c.1300, the core of the treatise is a collection of recipes and other art-technological instructions for, amongst other things, illuminating manuscripts. The anonymous tract offers a compilation of recipes seen in other works - where identifiable the recipes hail from Germany, Flanders, France, and Southern England - as well as new material. During the fourteenth century, various supplementary material was added, much of it from Italy, in the form of glosses and new recipes. Subsequently, the whole collection was recopied to become MS H277, with the original *Liber* and supplements now lost. Over two-thirds of the recipes contained are unique to this manuscript, making it a crucial study in the corpus of medieval illuminator techniques manuscripts.[23]

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[21] Grove Art Online, 'Theophilus - Grove Art Online', accessed 17 October 2020, https://www.oxfordartonline.com/groveart/view/10.1093/gao/9781884446054.001.0001/oao-9781884446054-e-7000084480.

[22] Theophilus, *On Divers Arts: The Foremost Medieval Treatise on Painting, Glassmaking, and Metalwork*, ed. John G. Hawthorne and Cyril Stanley Smith (New York: Dover Publications, 1979); Grove Art Online, 'Theophilus - Grove Art Online'.

[23] Clarke, *Mediaeval Painters' Materials and Techniques* p. 2.

De coloribus et artibus Romanorum

De coloribus et artibus Romanorum is an early medieval Latin treatise, written in Italy or northern Europe. The text is comprised of three books and is generally attributed to (H)Eraclius. He is likely the author of Book I and II, written sometime between the seventh and thirteenth century, and, although he is named as the author of Book III (which is a piecemeal collection added in the twelfth or thirteenth century), it is unlikely that he wrote this.[24]

The text can be found in two manuscripts (BL, Egerton MS. 840 A and Paris BnF MS. Lat. 6741), and both manuscripts also contain Theophilus' treatise *De diversis artibus*.

Roosen-Runge, mentioned in more detail below, demonstrated that the contents of the collection of recipes in *De coloribus et artibus Romanorum* correlates with many artistic practises in manuscript painting between the tenth and thirteenth century.[25]

Il libro dell' arte

Cennino Cennini's *Il libro dell' arte* is considered one of the most important texts in the history of the art of painting, although his text does not particularly relate to manuscript illumination.[26] Cennini, an Italian painter, was dead by 1427.

Alcherius

Alcherius' life details, including his profession, are patchy at best.[27] He is known to have lived in Milan until 1382, and then moved to Paris, collecting and recording recipes from both cities, as well as from artistic practitioners in Bologna, Genoa, and Venice. The recipe collection, compiled c. 1380-1420, is not solely a pigment preparation compendium, as could be said for previous works, but instead depicts a lively artistic milieu, where illuminators, artists and painters swapped ideas, thoughts and techniques.[28]

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[24] Grove Art Online, 'De Coloribus et Artibus Romanorum', accessed 3 October 2020, https://www.oxfordartonline.com/groveart/view/10.1093/gao/9781884446054.001.0001/oao-9781884446054-e-7000021764.

[25] Grove Art Online.

[26] Cennino Cennini and Lara Broecke, *Cennino Cennini's Il Libro Dell'arte: A New English Translation and Commentary with Italian Transcription* (London: Archetype, 2015).

[27] Rouse et al., *Medieval Manuscripts, Their Makers and Users*, p. 211.

[28] Nancy K. Turner, 'The Recipe Collection of Johannes Alcherius and the Painting Materials Used in Manuscript Illumination in France and Northern Italy, *c.* 1380-1420', *Studies in Conservation* 43 (1 January 1998), p. 45.

It seems that Alcherius often travelled around France and Italy, and the recipes in his collection are attributed to some of the foremost artistic practitioners of the time including recipes from, amongst others, Johannes of Modena (painter of the Bolognini Chapel frescos in Bologna) and the 'pictor supremus' of Milan Cathedral, Michelino da Besozzo.[29] This collection, therefore, indicates that in the generations before the recipes were recorded – around the same time as the manuscripts examined in this study were produced - there were advances and technological developments in the world of paint and pigment preparation which were shared and disseminated between the foremost practitioners across continental Europe. By 1431 Alcherius' recipe collection was in the hands of Jean Lebegue, who diligently copied the work, and added at least once recipe of his own.[30]

Merrifield

Mrs Merrifield published *Original Treatises dating from the XIIth to XVIIIth Centuries on the Arts of Painting* in 1849, and it has remained a core text in the field. [31] Of particular note to this study are the recipes recorded in Paris in 1398 by Alcherus, and later copied in 1431 by Jean Lebegue, as described above.

Thompson

Daniel Thompson (d. 1980) was a prolific researcher in the field of medieval pigments and published numerous studies on the subject that often form a starting point for today's enquiry. His overview *The Materials and Techniques of Medieval Painting* is probably his best-known work.[32]

Roosen-Runge

As Mark Clarke (himself detailed below) points out in his work *Really Don't Trust Your Eyes to Identify Medieval Manuscripts,* Roosen-Runge was a pioneer and expert in pigments in Medieval manuscripts.[33] Working in the 1960s, he considered many important manuscripts in the light of experiments on pigments recreated from recipe collections. He was able to make highly-educated

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[29] Turner, p. 45.
[30] Turner, p. 45.
[31] Merrifield, *Original Treatises: Dating from the XIIth to XVIIIth Centuries on the Arts of Painting, in Oil, Miniature, Mosaic, and on Glass; of Gilding, Dyeing, and the Preparation of Colours and Artificial Gems; Preceded by a General Introduction; with Translations, Prefaces, and Notes*; Mary P Merrifield, *Original Treatises on the Arts on Painting Volume 2* (New York: Dover Publications, 1967).
[32] Daniel V. Thompson, *The Materials and Techniques of Medieval Painting* (New York, NY: Dover Publ, 1956).
[33] Mark Clarke, 'Really Don't Trust Your Eyes to Identify Manuscript Pigments!', *Gazette Du Livre Médiéval* 44, no. 1 (2004), p. 50.

guesses as to the identification of pigments, using the only technology available to him at the time – a microscope. However, whilst many of his identifications are correct, many are also incorrect and have been 'discredited' by more modern methods of analysis.[34]

Mark Clarke

Mark Clarke is a technical art historian, currently at the Universidade NOVA de Lisboa, who specialises in researching, translating, and interpreting artists' technical craft books, such as *The Montpellier Liber diversarum arcium.*[35] He has published numerous books and papers on medieval art recipe books.[36]

Pigments, Dyes and Lake Pigments

A pigment (usually derived from a mineral source) is insoluble in water, whereas a dye (usually from an organic source) is soluble, and so has to be suspended in water or an oil-based binder before use. A lake pigment is a dye attached to a colourless insert substrate allowing the dye to be used as a pigment. A dye deployed alone, whether a juice or a decoction, would not have had the covering power or opacity necessary to provide the colour needed for manuscript artwork. In the Middle Ages, lake dye-infused material, known as clothlets, was imported and the colour removed into solution with alkaline lye made usually from wood ash or urine. This had clear implications for the dye industry - colours could be imported, traded or purchased and employed to dye cloth with relative ease. For manuscript production, the dye might have been of sufficient colour to be deployed as a glaze or stain when added to a binder. If not, the dye could have been made into a lake pigment. In this case, coloured lye was added to a vat that contained alum (or some other mordant, usually a metallic salt). When alkaline lye and the acidic alum react, aluminium hydroxide forms; this compound is inert and colourless in itself but is coloured by the entrapped dye. The dried coloured aluminium hydroxide could then be treated as if it were a pigment. This process was well known, and medieval recipe collections provide very detailed instructions on these methods. However, that is not to suggest that producing lake pigments was easy - it involved boiling vats of powerful chemicals. The term 'lake' now refers to any coloured lake pigment, but in the Middle Ages 'lake' was reserved for red colours.[37]

Unlike most inorganic pigments, many dyes are not lightfast when used to colour clothing, nor when made into lake pigments. This phenomenon was well known during the medieval period and thus

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[34] Clarke, pp. 50-53.

[35] Clarke, *Mediaeval Painters' Materials and Techniques*.

[36] FCT/UNL, 'Mark Clarke', accessed 21 December 2020, https://www.dcr.fct.unl.pt/pessoas/professor-auxiliar-convidado/mark-clarke.

[37] Philip Ball, *Bright Earth: The Invention of Colour* (London: Vintage, 2009), p.108.

explains the limited deployment of lake pigments in manuscripts. As later chapters attest, the identification of organic substances, such as those found in lake pigments, i.e. dyes, is difficult to ascertain in illuminations, with non-invasive technologies.

In the following sections information regarding scientific analysis techniques of certain pigments and dyes are included for reference. More details about the exact nature of these processes will follow in Chapter Three.

Reds, Oranges and Pinks

Red is a colour that has been used by humans for millennia; many reds occur naturally in the earth. Vibrant reds, the colour of blood, through to softer pinks for skin tones, are seen frequently in medieval manuscripts. Some were employed in their natural form and required little processing from ground to page - Armenian bole for example. A few red pigments, like ochres, required simple preparation such as washing and roasting. Others were synthetic and the result of complex alchemical reactions.

In manuscripts, red is used for both text and artwork. Red text (rubric) is designed to stand out from the black ink and parchment of the page and is often employed to orientate the reader. In images, its deployment can be prosaic - for lips or clothing, for example - or it can be deployed to symbolise the blood of Christ.

Cinnabar and vermilion

Cinnabar is naturally occurring mercury (II) sulphide (HgS) and is the principal ore for elemental mercury or quicksilver. It has been discovered in burial sites dating from before 3000 BCE in Europe, where its remarkable purity was probably achieved by a combination of grinding and levigation.[38] It was a pigment well known to the Ancient Romans and Ancient Greeks but was seemingly unknown in Ancient Egypt. In Roman times and the Middle Ages, it was mined at Almaden in Spain and in Sinope, a port near the Black Sea, through which it was no doubt traded.

Cinnabar's pure and intense colour, good hiding power, stability, and ease of use, together with its limited supply, meant that it was expensive. Therefore vermilion, cinnabar's synthetic equivalent, became increasingly popular. The name vermilion is derived from the Latin 'vermes', a name originally

[38] Jesus Martín-Gil et al., 'The First Known Use of Vermillion', *Cellular and Molecular Life Sciences CMLS* 51 (1 September 1995), p.760.

linked with kermes, an insect employed in the preparation of red dye (described below). Crimson and carmine are also words derived from kermes.

A recipe for the synthesis of vermilion can be found in Theophilus' tract *De diversis artibus*, as well as manuscripts from The Mappae Clavicula tradition.[39] In addition, the pigment's alchemical nature was noted in Cennini's recipes, although no details are provided, probably partly because its manufacture was so widespread by this point that there was no merit in recording it.[40]

Recipes centre on the fact that, when elemental sulfur and elemental mercury are mixed a black substance is formed, which when heated or sublimed produces the desired red pigment. What is reported here are two forms of the tri-morphism of mercury (ii) sulfide - metacinnabar forms at low temperatures and is black, and from this, the desired red form - cinnabar - can be obtained. Hyper-cinnabar, the third type, is unstable and not seen in nature. It forms at higher temperatures and is also black.

As it was highly sought after, Cennini suggests that vermilion sometimes had brick dust and red lead added along the trade route as an extender, perhaps by unscrupulous merchants or by economical workshops.[41]

Team Pigment have identified vermilion in a sixth-century Italian manuscript associated with St. Augustine of Canterbury (CCCC MS 286).[42] It has also been identified in Cambridge Corpus Christi College MS 411, an English manuscript dating from the end of the tenth/start of the eleventh century. In England and France, it is found in occasional manuscripts from this time onwards and is then seen regularly from the middle of the eleventh century, displacing red lead as the standard red in English Illumination, with almost every manuscript dated afterwards up to the advent of print containing the pigment.[43] Another example of eleventh-century use is seen in a manuscript made in Bavaria, MS McClean 20, in the Fitzwilliam collection. A late sixteenth-century example of its deployment can be seen in the Marlay Cutting It. 40, from the Fitzwilliam Museum.[44]

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[39] Ashok Roy and National Gallery of Art, eds., *Artists' Pigments: A Handbook of Their History and Characteristics*, vol. 2 (Washington, DC: National Gallery of Art, 2012), p. 162.
[40] Panayotova et al., *Colour*, p. 109.
[41] Panayotova et al., p. 109.
[42] Andrew Beeby, Richard Gameson, and Catherine Nicholson, 'New Light on Old Illuminations', *Archives and Records*, 22 May 2017, p. 250.
[43] Beeby, Gameson, and Nicholson, p. 248.
[44] Panayotova et al., *Colour*, p. 28.

Vermilion is usually easily distinguished by its characteristic Raman spectrum – under 633 nm excitation, it exhibits an extremely strong band at 251 cm^{-1}, and a smaller band at 342 cm^{-1} as can be seen in the sample spectra in Figure 3. Traces of the mineral can be seen at exceptionally low powers despite fluorescence, as it is such a strong Raman scatterer. The FORS spectrum of vermilion has an inflection point at 600 nm, as seen in Figure 4, and shows absorption in the blue and green regions of the spectrum, although there are no further characteristic bands in the IR region.[45] XRF can identify the presence of mercury, which can be diagnostic as no other pigments contain this element. It is difficult to tell vermilion and cinnabar apart analytically.[46]

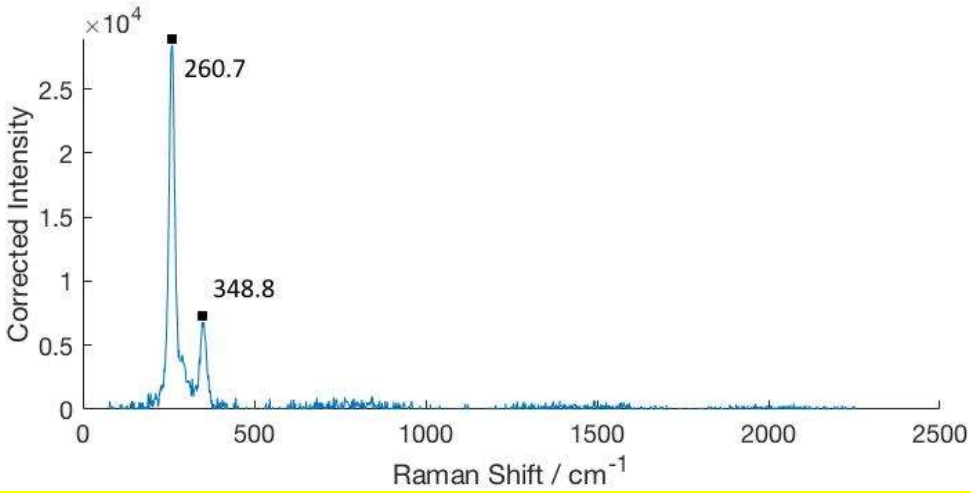

Figure 3: A sample Raman spectrum of vermilion.

[45] Maurizio Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', *Analytical Methods* 6, no. 5 (2014), p. 1488.
[46] Panayotova et al., *Colour*, p. 27.

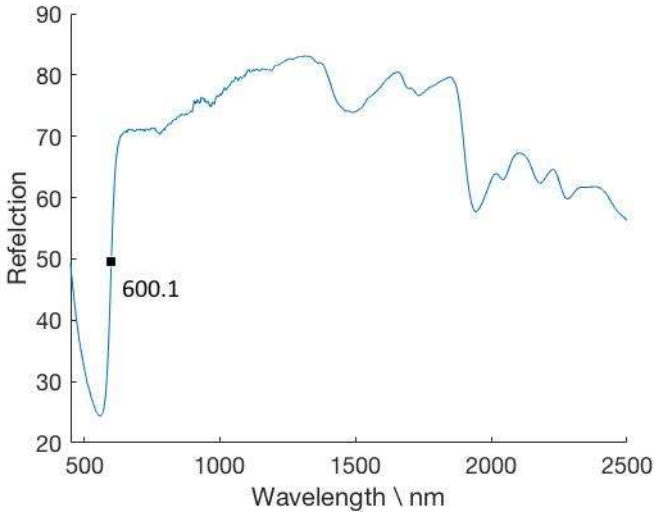

Figure 4: A laboratory sample spectra of vermilion.

Vermilion can degrade to calomel (mercury (I) chloride), although this is not as commonly seen as the degradation to metacinnabar (mercury sulfide).[47] Calomel can be observed as a white crust whilst mercury sulfide, more commonly observed, is a black patina on the surface of the pigment area.[48] It has been reported that calomel was intentionally deployed in a fifteenth-century English manuscript – the Fitzwilliam Missal (Fitz MS 34) – the earliest known use.[49]

Minium, Litharge, Red Lead and Massicot

The yellow-orange pigment litharge (PbO) is a naturally occurring lead oxide, deposits of which have been found in Lower Saxony in Germany and Derbyshire in England. This pigment may oxidise further to produce a bright orange lead tetraoxide – known as minium (2PbO.PbO2 – historically known as Pb_3O_4). Although this oxidation can occur naturally, it is extremely rare.

Minium has a synthetic equivalent, red lead, which is made by roasting and agitating powdered white lead (described further below) or litharge in the presence of oxygen, a technology that was employed in Ancient Rome.[50] Red lead was also a by-product of the process whereby silver was extracted from galena (lead ore).[51] This process produces a vibrant and stable, optically dense orange-red pigment

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[47] *Technical Bulletin. Vol. 23.* (London: National Gallery, 2002), p. 54.

[48] Roy and National Gallery of Art, *Artists' Pigments*, p. 167.

[49] Mila Crippa et al., 'New Evidence for the Intentional Use of Calomel as a White Pigment', *Journal of Raman Spectroscopy* 52, no. 1 (2021): 15–22.

[50] Nicholas Eastaugh, ed., *The Pigment Compendium: A Dictionary of Historical Pigments* (Amsterdam; Boston: Elsevier Butterworth-Heinemann, 2004), p. 235.

[51] Panayotova et al., *Colour*, p. 60.

used extensively in western manuscripts from late antiquity to the sixteenth century. It has been reported that the particle size of red lead affects its colour, which would suggest that the more finely ground the pigment is, the redder its hue.[52]

This manufacturing process can easily go slightly awry: if insufficient oxygen is present during the processing, then massicot (PbO), a yellow material, forms. This can be readily detected as a contaminant in red lead by Raman spectroscopy with bands at 143 and 290 cm^{-1}. Of course, this effect may have been induced deliberately at times, in order to produce different hues. The presence or absence of massicot in an area of red lead, therefore, can tell us something of the skill of the people preparing the pigment. Furthermore, the original lead oxide, litharge, may be a contaminant present after manufacture in crude conditions, where not enough heat has been produced to allow the oxidation process to occur.[53] These permutations in the manufacturing process have been replicated and examined by Clark et al. who found that the differing contaminants produced can be identified by Raman spectroscopy.

Red lead reacts easily with sulfides in the air, or released from degradation of parchment, to form PbS, which is seen as a dark grey patina on the surface of what would formerly have been a bright orange area. Alternatively, the pigment turns a brown colour, which is noticeable, especially in books from the later Middle Ages.

The FORS spectrum of the pigment, which is a semi-conductor, reveals an inflection point at 580 nm as seen in Figure 5, although the spectra cannot identify contamination.[54] Thus, red lead is better identified by a series of peaks in the Raman spectrum with strong bands at 121 and 549 cm^{-1} under 633 nm excitation, as seen in Figure 6.[55] Massicot, if present, can be seen in bands at 124 and 285 cm^{-1}. XRF can identify the presence of lead, but does not identify the chemical composition of the pigment or its contaminants.

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[52] Robert L. Feller, ed., *Artists' Pigments: A Handbook of Their History and Characteristics.*, vol. 1 (New York: Oxford Univ. Press, 1986) p. 114.

[53] Eastaugh, *The Pigment Compendium*, p. 235.

[54] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry' p.1488.

[55] G. Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', *Analytical Methods* 10, no. 10 (2018), p. 1222.

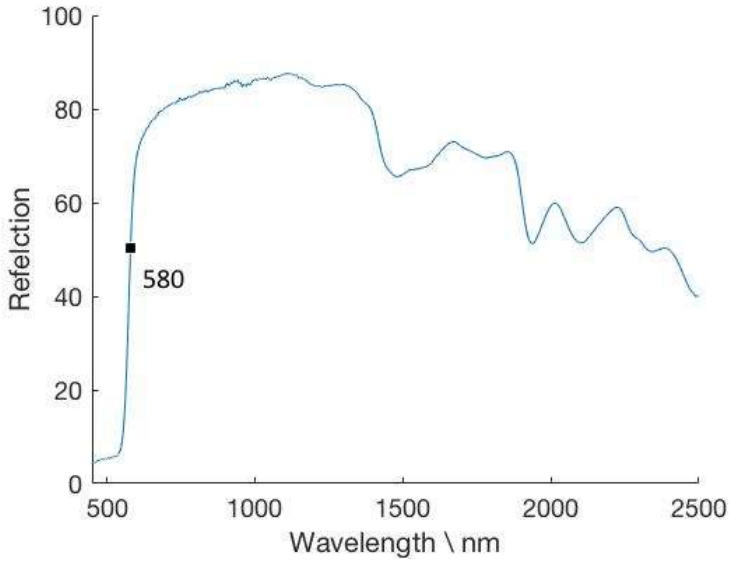

Figure 5: A laboratory sample spectra of red lead.

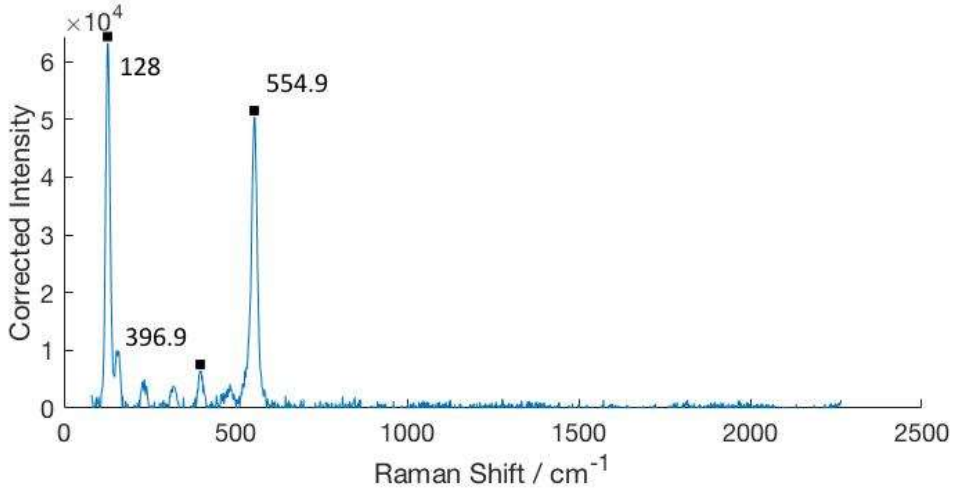

Figure 6: A sample Raman spectrum of red lead.

Red lead has been found by Team Pigment in the sixth-century Gospels of Augustine (CCCC MS 286), where it is ubiquitous. Another early use of red lead is in DCL A.II.10, a mid-seventh century manuscript, also examined by Team Pigment.[56] It is present in most early Northumbrian books. The colour can be found in most manuscripts subsequently. Interestingly, the earliest books examined tend to display more pristine red lead, whereas in later books (a sixteenth-century example is seen in

[56] Richard Gameson, Andrew Beeby, and Catherine Nicholson, 'Pigments of the Earliest Northumbrian Manuscripts', *Scriptorium* 69 (2015), p. 38.

the Fitzwilliam Museum Marlay Cutting It. 40, for example) the pigment is often contaminated.[57] This taint may be due to the nature of larger-scale manufacture of the colour, or it could be that this was the desired effect.

Massicot

Despite generally assumed to be a contaminant in the production of red lead when heated from white lead, massicot is occasionally deployed as a pigment in its own right. It is sometimes chemically confused with litharge, another lead oxide mineral pigment. Massicot (PbO) is yellow, orthorhombic and a high-temperature polymorph of litharge (PbO), which is yellow and tetragonal, and fairly unstable. Aside from the chemical confusion, the name massicot can be muddled with lead-tin yellow - both contain lead and are yellow, and have been confused in some recipe collections.

Massicot is best identified by its Raman spectrum with peaks at 142 and 288 cm^{-1} as seen in Figure 7.[58] It is not always easy to distinguish between massicot, litharge, and red lead. An identification of massicot in a Botticelli painting has been disputed as being caused by the Raman laser heating the surface and causing head induced lead IV oxide or lead sulfide degradation.[59] When working with cultural artefacts Team Pigment keep Raman laser power < 0.5 mW μm^{-2} in order to avoid this problem. Furthermore, it is not always possible to tell whether massicot is present as a contaminant or as a deliberate artistic choice.

[57] Panayotova et al., *Colour*, p. 55.

[58] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

[59] Eastaugh, *The Pigment Compendium*, p. 262.

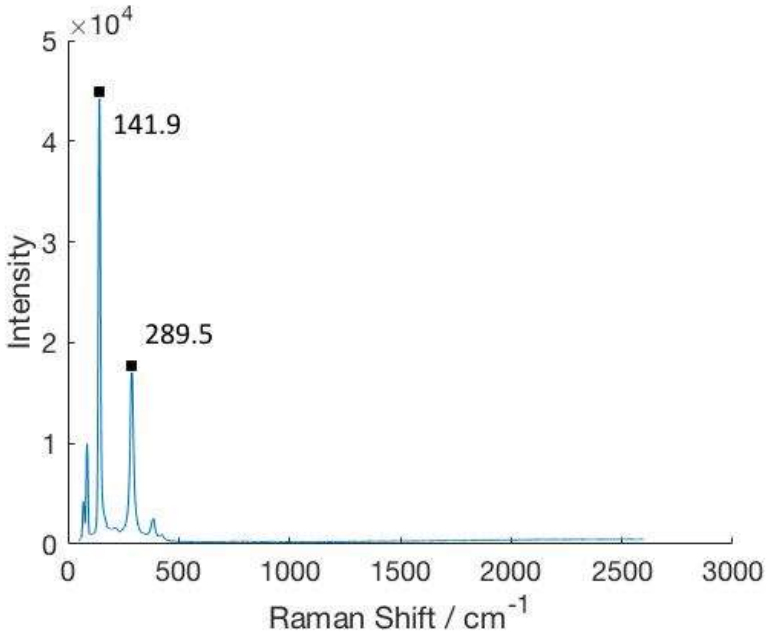

Figure 7: The Raman spectrum of a laboratory sample spectrum of massicot.

Team Pigment have found many cases where massicot has been present in red lead - assumed to be a contaminant due to the nature of the colour. Massicot has also been found deployed as a yellow pigment in its own right in the Spicer Hours, a late fifteenth-century English manuscript.[60]

Red Earths

Red earths, rich in iron, can be found all over the world and can be deployed as a pigment with very little preparation, it may be only washed or roasted or both. Armenian bole, a type of red clay, was used extensively as preparation for gold leaf, being made into a mound on which the leaf was laid.[61] Red ochres and haematite, as well as burnt sienna and burnt umber, are all similar pigments that fall into the category of red earths, with iron providing the red-brown chromophore.

Iron oxides can be identified from their Raman spectrum with a main peak at 408 cm^{-1}. When examined with FORS, ochres tend to give a characteristic spectrum due to the presence of haematite (Fe_2O_3) as a chromophore - an inflection points at around 580 nm and 700 nm, as seen in Figure 8, plus an absorption band at around 850 nm.[62]

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[60] The Spicer Hours were examined whilst at Sam Fogg, an art dealership in London. I am unable to ascertain their current whereabouts.

[61] Panayotova et al., *Colour*, p. 21.

[62] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1488.

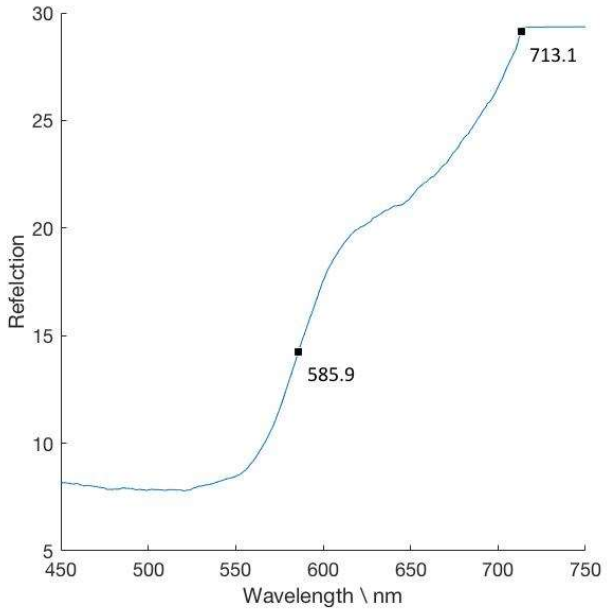

Figure 8: A FORS spectrum of a laboratory sample of iron oxide (visible wavelengths only).

One instance of the deployment of red ochre, in this case, iron oxide, was seen was in The Lindisfarne Gospels where Aldred, a cleric, employed red earth to gloss the latter part of the text with Old English whilst at Chester-Le-Street, in about 970 CE. Its use is an intriguing contrast to the rest of the gloss, which is on black-brown ink. The ochre was likely obtained locally from an iron-rich ore, such as haematite.[63]

Lac

Lac (sometimes known as sticklac) is produced by tiny insects from the genus *Kerria,* which secrete a red resin as part of their cocoon. The red mass is created by thousands of these small parasites and is found on the twigs and branches of trees in southern and south-east Asia. This resinous material can be treated in several different ways; the lac dye, the part which gives the colour, makes up only 10% of the resin, with the rest being made up mainly of different laccaic acids.[64] Lac can be made into a

[63] Andrew Beeby et al., 'Aldred's Red Gloss', *The Lindisfarne Gospels*, 15 June 2017, p. 204.

[64] Rita Castro et al., 'Combining SERS and Microspectrofluorimetry with Historically Accurate Reconstructions for the Characterization of Lac Dye Paints in Medieval Manuscript Illuminations: Combining SERS and Microspectrofluorimetry with Reconstructions', *Journal of Raman Spectroscopy* 45 (November 2014), p.1172.

lake pigment; indeed, it is this substance that lends its name to the concept.[65] Lac is also the principal ingredient in shellac.

Kermes

Kermes was a popular choice for insect pink until the 1520s when it was replaced by cochineal (see the section on modern pigments below).[66] The red dye is derived from the insect *Kermes vermilio*, which is native to the Mediterranean and lives on the sap of the Kermes oak. The dye has been used since antiquity and was often called 'grain', with cloth 'dyed in the grain', the granular texture owing to the desiccated bodies of the insects and eggs.[67] In medieval Europe, kermes was used primarily for producing scarlet cloth. Kermes can be made into a lake (carmine lake), although this process is difficult and was probably not perfected until after the fifteenth century. Therefore, its deployment in earlier medieval manuscripts is most likely limited to glazes or mixtures.[68]

Madder

The use of the dye extracted from the root of the madder plant *Rubia tinctorum*, produces, as its name suggests, a red/pink colourant that has been employed since antiquity. It was utilized particularly for colouring cloth and leather, but also as a lake pigment. Roman use of madder lake has been seen in Romano-Egyptian works of art dating from the first century CE.[69] It has been detected in few manuscripts - one purported use is in an illustrated volume dating from the late 1400s in the Advocates Library, Edinburgh.[70] Although not lightfast, it is more stable under natural illumination than kermes or lac, but it is also more difficult to make.[71]

Alizarin, the principal colourant of madder (along with purpurin and pseudopurpurin), can be created artificially today and is typically deployed as a transparent but rich coloured glaze. Altering the chemistry of the substrate can produce madders of different hues, including purple.[72]

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[65] Merriam-Webster Dictionary, 'Definition of "Lac"', accessed 12 June 2020, https://www.merriam-webster.com/dictionary/lac.

[66] Panayotova et al., *Colour*, p. 30.

[67] D. T. Jenkins, ed., *The Cambridge History of Western Textiles* (Cambridge, U.K.; New York: Cambridge University Press, 2003), p. 214.

[68] Ball, *Bright Earth*, p. 107.

[69] Getty Museum, 'The Matter of Madder in the Ancient World', 25 August 2020, https://www.getty.edu/publications/mummyportraits/part-one/3/.

[70] Elisabeth West FitzHugh, *Artists' Pigments: A Handbook of Their History and Characteristics*, vol. 3 (Washington: National Gallery of Art, 2012), p. 111.

[71] Ball, *Bright Earth*, p. 108.

[72] FitzHugh, *Artists' Pigments: A Handbook of Their History and Characteristics*, p. 41.

Brazilwood

Brazilwood *Caesalpinia echinata* yields a red dye when shredded and boiled, and was utilised as a lake pigment called 'roset' in England in the later Middle Ages. *Caesalpinia braziliensis*, whose roots are similarly employed, reached medieval Europe from Ceylon via Alexandria and was a much cheaper alternative to kermes.[73] With the 'discovery' of the Americas, the dye was obtained from *Caesalpinia crista* - native to Jamaica and, of course, Brazil.

Despite Thompson's claims that this colour was one of the foremost colourants of the Middle Ages, it has not been identified in many manuscripts, although it has been found in some fifteenth-century French books of hours, where it was used as a glaze.[74] It was a colour banned from some dyers' guilds as being too prone to fading.[75] Its use as a lake-pigment, therefore, would have been limited.

Pinks

Pinks could be made by simply mixing two mineral pigments, a white pigment- chalk, gypsum, or white lead - with a red one - vermilion or red lead. However, the red component of most pinks seen in manuscripts is derived from organic sources - perhaps lakes of madder, kermes, lac or Brazilwood. It may be that organic and mineral substances were mixed together, or that organic dyes provided a colour-changing glaze when applied over a mineral mixture. A common problem amongst lake pigments is that they are not lightfast, meaning their usage in paints in manuscripts was probably limited.

Yellow and Orange

Yellows are found often in nature, but finding a stable and lightfast yellow that could provide the strong colours and hiding power desired for manuscript artwork was often difficult. As a result, many manuscripts contain no yellow colourants.

Where used, yellow was deployed both as a colour in its own right and also as a surrogate for gold. It has occasionally been found underneath gold, either as an attempt to provide the gold with more 'gleam', or to provide a similar coloured background should the gold scale off. In Durham Cathedral

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[73] Ball, *Bright Earth*, p.107.
[74] Maria João Melo et al., 'A Spectroscopic Study of Brazilwood Paints in Medieval Books of Hours', *Applied Spectroscopy* 68, no. 4 (April 2014), p. 434.
[75] Ball, *Bright Earth*, p. 107.

Library C.II.6, for example, which is an Italian law book from the thirteenth century, orpiment was painted under the gold.

Orpiment

Perhaps the most frequently seen mineral yellow in manuscripts is orpiment - a bright yellow compound found around volcanic outlets and hot springs throughout the world. Traded during the Roman Empire, it was also imported during the Middle Ages from Italy, particularly from the Bay of Naples and the Aeolian volcanic islands, and as a sought-after pigment, it was expensive.[76] Mineral orpiment is often found alongside realgar and pararealgar, which are detailed below. Orpiment's bright golden hues mean that it was frequently deployed as an alternative to gold - in fact, the name orpiment is derived from auripigmentum (pigment of gold).

Orpiment is arsenic (III) sulfide and, as might be expected, is highly toxic. It is also fairly reactive – reacting with red lead to form PbS, and causing silver to tarnish. The tenth-century section of *De coloribus et artibus Romanorum*, a composite text that travelled under the name '(H)Eraclius' (described above), states that orpiment does not work well with many colours, including folium, any green, and minium. As most greens were copper-based (see the section on green below), this is a reasonable assertion - the copper would have reacted with the sulfur in orpiment to make black copper sulfide.[77]

Noting its toxicity, Cennini favoured the use of artificial orpiment procured from experts in its manufacture.[78] Artificial orpiment was made by reacting H_2S with AsO_3, or by subliming equal amounts of arsenic and sulfur. Arsenic smelters do not appear in Europe before the fourteenth century, and it is unlikely that the knowledge of how to make artificial orpiment was around much before then. Indeed, if it was, then the lacuna in orpiment use in England during the High Middle Ages is even harder to explain.

Team Pigment have found orpiment in manuscripts dating from the seventh century - in DCL A.II.10 for example - and the pigment was employed as a staple in several Northumbrian manuscripts dated before the tenth century.[79] A chronological study of Canterbury-made manuscripts shows that orpiment use in the tenth century was rare and intermittent in the eleventh and twelfth centuries. It was not deployed in some of the most lavish twelfth-century manuscripts where it might have been

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[76] Eastaugh, *The Pigment Compendium*, p. 291.
[77] Ball, *Bright Earth*, p. 300.
[78] Panayotova et al., *Colour*, p. 110.
[79] Gameson, Beeby, and Nicholson, 'Pigments of the Earliest Northumbrian Manuscripts', p. 33-59.

expected.[80] Its use in the thirteenth century is very limited, its yellow tones replaced with lavish employment of gold.

As it scatters the Raman laser very strongly, orpiment is best identified in manuscripts by its Raman spectrum, which shows characteristic peaks at 354 and 309 cm^{-1} under 633 nm excitation, as seen in Figure 10 and Figure 9. In a FORS spectrum, its identifying feature is an inflection point at around 480 nm, although this is not diagnostic. XRF identifies the presence of sulfur and arsenic in this material, although it cannot discern between orpiment, realgar and arsenic sulfide glass.

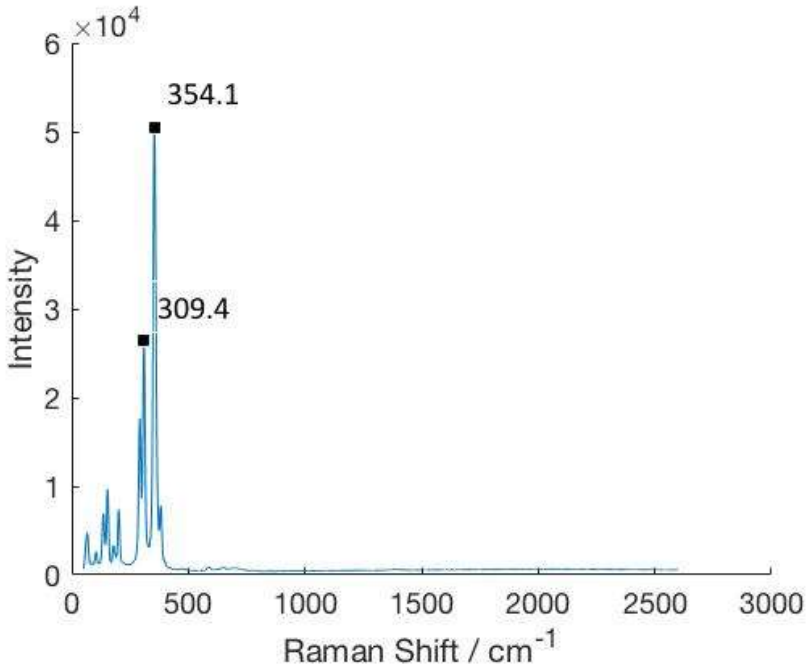

Figure 9: The Raman spectrum of a laboratory sample of orpiment.

Realgar, Pararealgar and Arsenic Sulfide Glass

A slightly more orange yellow, called realgar (arsenic (II) sulfide (α-As_4S_4), is often found alongside orpiment in volcanic regions. In *De Natura Fossilium*, Agricola (1556) says that realgar can be made from orpiment by heating it in a sealed crucible for five hours. Pararealgar (ß-As_4S_4), which can be

[80] Richard Gameson, Andrew Beeby, and Catherine Nicholson, 'Colour at Canterbury', in *Manuscripts in the Making: Art and Science*, vol. 1 (Harvey Miller Publishers, 2018), p. 24.

bright yellow, orange yellow, or brown yellow, is the light-induced degradation phase of realgar. Both pigments are toxic.[81]

Like orpiment, realgar and pararealgar are identified by Raman spectroscopy. Realgar has strong peaks at 193 and 221 cm^{-1} that have been attributed to the bending of S-As-S and a very strong peak at 353 cm^{-1}, which is attributed to the stretching vibration of As-S. A sample spectrum can be seen in Figure 10.

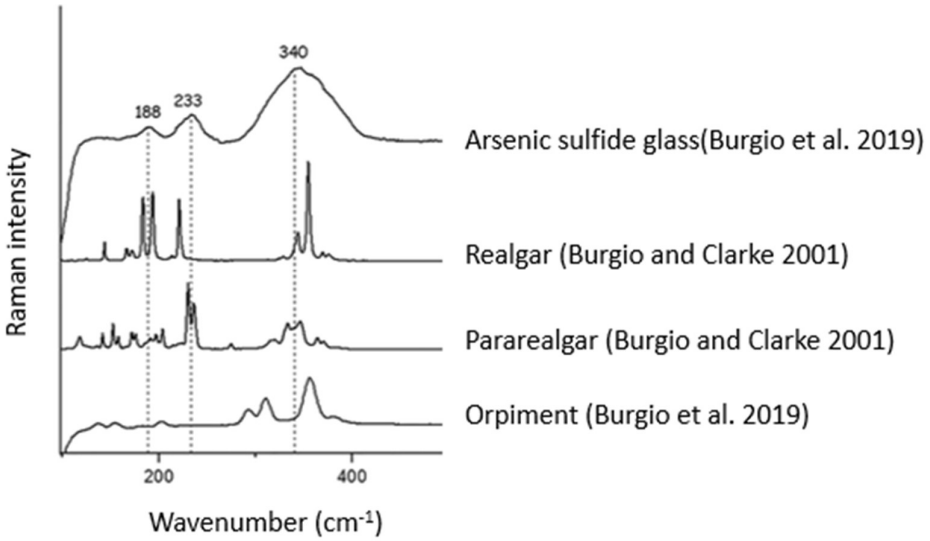

Figure 10: A comparison of the Raman spectra of the arsenic yellow/orange pigments. Adapted from Burgio et al (2019).[82]

Pararealgar has very strong peaks at 230 and 345 cm^{-1} attributed to As-As-As symmetric stretching vibrations and at 236 and 345 cm^{-1}, which have been identified as asymmetric vibrations. These natural pigments have been rarely identified in manuscripts, and so their use through the centuries is difficult to ascertain.[83] Due to the photolabile nature of realgar, it is imperative that a weak laser is used (<0.5mWcm^{-1}) in order to avoid photodegradation. FORS identification of the pigment utilises an inflection point at 530 nm, although the molecular nature of the substance cannot be identified. XRF

[81] Panayotova et al., *Colour*, p.28; Marc Vermeulen et al., 'Identification by Raman Spectroscopy of Pararealgar as a Starting Material in the Synthesis of Amorphous Arsenic Sulfide Pigments', *Dyes and Pigments* 149 (1 February 2018), p.295.

[82] Lucia Burgio et al., 'Orange for Gold? Arsenic Sulfide Glass on the V&A Leman Album', *Journal of Raman Spectroscopy* 50, no. 8 (August 2019): 1169–76, p. 5.

[83] Vermeulen et al., 'Identification by Raman Spectroscopy of Pararealgar as a Starting Material in the Synthesis of Amorphous Arsenic Sulfide Pigments', p.291.

can reveal the presence of arsenic and sulfur but again cannot reveal the molecular format of the pigment, and therefore its state of degradation. A comparison of the Raman spectra of the arsenic-based pigments is shown below in Figure 10.

Team Pigment identified realgar in the Bodleian Library's twelfth-century Auct. E. Inf. 1-2 Bible, from Winchester, where it was used sparingly as decoration over gold. Interestingly, pararealgar was observed on one folio of this manuscript that had been on exhibition over several years. It seems likely that the folio had been exposed to UV light during its years on display, presumably inducing the change from realgar to pararealgar.

Arsenic sulfide glass is a bright orange pigment g-$AS_{40}S_{60}$. The glass part of the name is somewhat of a misnomer in that the pigment is not derived from glass making, like smalt (see below) but comes from the fact that it is a chalcogenide glass - an amorphous solid. The technology and methods for producing arsenic sulfide glass are not well known - like the production of vermilion, there is a wet process which was not thought to have been discovered until the nineteenth century, and a dry process that was described by Cennini around 1400 CE. Arsenic smelters were not thought to have been developed in Europe until the fourteenth century, so it is unlikely that arsenic sulfide glass was around before this time. According to recipes, the pigment results from the sublimation of an arsenic oxide or orpiment with or without the addition of sulfur. From the fifteenth century onwards, there is much documentary evidence for an extensive trade in synthetic arsenic sulfides.[84]

Team Pigment have identified this substance, characterised by its very strong and broad peak attributed to the As-S-As stretching vibration in the Raman spectrum at 341 cm^{-1}, in the artwork on one folio in *Les Cent Nouvelles Nouvelles* (Hunter 252) at Glasgow University Library. *Les Cent Nouvelles Nouvelles* is a fifteenth-century French manuscript of a medium grade. It seems unlikely here that the use of the uncommon bright orange arsenic sulfide glass is symbolic, and its deployment is probably just happenstance.[85] The substance has also been identified in two Fitzwilliam Museum works c. 1500 - a French manuscript, MS 159, and an Italian manuscript cutting, It. 25.[86]

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[84]Günter Grundmann et al., 'The Rediscovery of Sublimed Arsenic Sulphide Pigments in Painting and Polychromy: Applications of Raman Microspectroscopy', 2011 in Marika Spring, ed., *Studying Old Master Paintings: Technology and Practice: The National Gallery Technical Bulletin 30th Anniversary Conference Postprints* (London: Archetype Publications, 2011), p. 269

[85] Richard Gameson et al., 'Les Cent Nouvelles Nouvelles: The Physical Fabric of the Fables', (Forthcoming) Please note that L. Garner is named on this paper.

[86] Panayotova et al., *Colour*, p. 190 and p. 326.

Yellow Earths

Yellow colours can be obtained from naturally forming earth pigments that are found in soil, or through weathering of rocks. Many British yellow ochre deposits, such as the Shotover ochres from Oxfordshire, have been exhausted. Other yellow ochre deposits are in Southern England - Bury St. Edmunds and The Forest of Dean. There were likely many other now unknown deposits too – just as with red ochres, local supplies would not have been documented and were probably exploited until exhausted.[87] Other important deposits that may have been part of the trade market in the Middle Ages are in France and Greece.

Yellow ochres, goethite, natural sienna, and natural umber are all classed as yellow, and roasting them can produce darker brown, red and violet shades. This technology has been available since the Palaeolithic period; ochre deposits are frequently found in rock and cave art. Like red ochres, yellow ochres are distinguished by their FORS spectrum, which exhibits two inflection points. A polymorph of the mineral goethite (FeO(OH)) provides the chromophore in many cases.

Saffron

Saffron (*crocus sativus*) has such an intense colour that it could be placed directly into a binder to be deployed as a glaze or stain, although its propensity to fade in sunlight probably limited its employment.[88] High-quality saffron was probably imported from Persia, where it was grown commercially from the tenth century, perhaps less for its nature as a colourant but more as a spice. Its expense came not only from being an import but was also due to the intense cultivation and processing needed to produce the powder - the stamens of 4,000 crocuses would have yielded only one ounce. Saffron was also grown in Europe, particularly in Spain, and Italy, especially in Sicily. In Britain, the town of Saffron Walden was also an important source, as its name suggests. Merrifield states that a French recipe book dating from around 1300 describes French saffron as not 'the perfect sort'.[89]

Saffron could be made into a lake pigment, and Cennini states that when combined with azurite, its lake makes an excellent grass green vergaut.[90] Saffron has properties that mollify the caustic

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[87] Panayotova et al., p. 60.
[88] Clarke, *Mediaeval Painters' Materials and Techniques*, p.186.
[89] Panayotova et al., *Colour*, p. 60.
[90] Ball, *Bright Earth*, p.300.

properties of verdigris and other copper greens and thus was employed as a buffer between these pigments and the page.[91]

Lead-tin yellow

A bright yellow manufactured pigment, lead-tin yellow can be made by heating lead oxide with metastannic acid at high temperatures. There are two types of lead-tin yellow, lead-tin yellow Type I, is Pb_2SnO_4, and Type II, which is similar to the first but contains silica. They can be identified by their differing Raman spectra. The Ancient Romans employed lead-tin yellow in their glass-making, which is likely to be how the second type was discovered. Lead tin yellow seems to have been a pigment created and employed in Europe - it is not seen in other places and cultures unless there is evidence of trade with Europe.[92]

Lead tin yellow has been discovered in paintings from around 1300 - Giotto's *Madonna and Child,* in the Samuel H. Kress Collection at the National Gallery of Art, Washington DC (1939.1.256), is one example.[93] It was employed routinely in the fifteenth, sixteenth and seventeenth century in paintings, but intriguingly disappears from use during the eighteenth century.[94]

That the colourant is deployed in manuscripts with increasing verve in the later Middle Ages is not a surprise: once made, it is a stable and bright pigment with good hiding power. It is fairly unreactive and was often used to make green when mixed with blue, or to lighten green foliage, as well and being employed on its own.

The pigment can be deduced by its Raman signal, which gives bands at 130, 196 and 455 cm^{-1} for type I, as shown in Figure 11, and 77, 127 and 193 cm^{-1} for type II.[95]

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[91] Panayotova et al., *Colour*, p. 29.
[92] Eastaugh, *The Pigment Compendium*, p. 239.
[93] Barbara H. Berrie, Marco Leona, and Richard McLaughlin, 'Unusual Pigments Found in a Painting by Giotto (c. 1266-1337) Reveal Diversity of Materials Used by Medieval Artists', *Heritage Science* 4 (December 2016), p. 1.
[94] Ball, *Bright Earth*, p. 340.
[95] Radka Šefců, Štěpánka Chlumská, and Alena Hostašová, 'An Investigation of the Lead Tin Yellows Type I and II and Their Use in Bohemian Panel Paintings from the Gothic Period', *Heritage Science* 3, no. 1 (11 May 2015): 16, p. 4; Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1223.

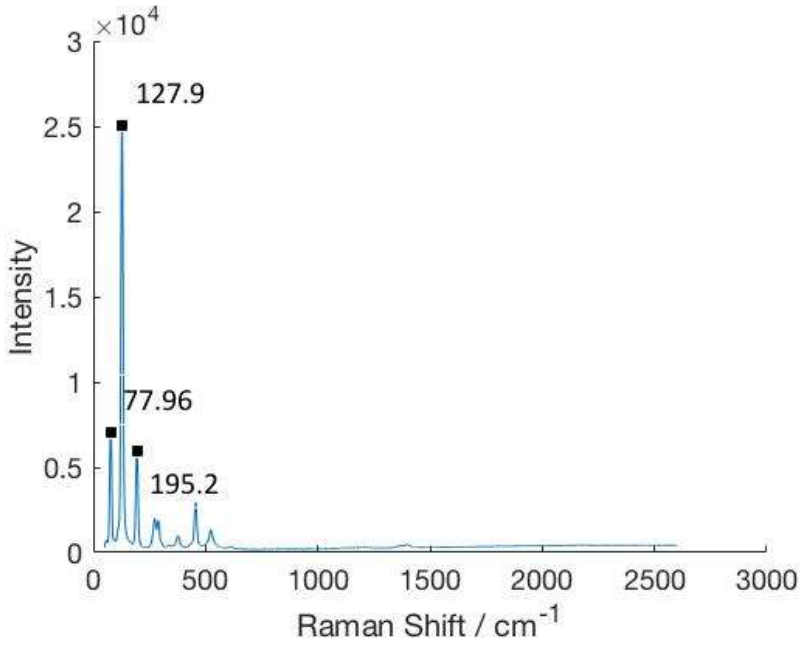

Figure 11: A laboratory sample Raman spectroscopy spectrum of lead tin yellow type one.

Weld

A lake pigment made from the weld plant *Reseda luteola*, known as or the dyer's herb or fuller's weed, was sometimes employed as an alternative to orpiment but was not lightfast.[96]

Blue

Until the eighteenth century before the synthesis of Prussian blue and cobalt blue ($CoAl_2O_4$), the colours described in detail below were frequently employed. The colour is associated with the sky, sea, and water, but also with heaven and the divine. The Virgin Mary is often depicted with a blue robe or cloak, and Jesus is frequently clothed in blue. Blue was an expensive colour, and the deployment of different blue pigments can reveal something of the motivations of the artists or workshops creating the manuscripts.

Azurite

Azurite ($Cu_3(CO_3)_2(OH)_2$) is a naturally occurring hydrated copper carbonate pigment, shown in its mineral form in Figure 12. Found in copper ore deposits in Germany and Hungary, as well as near Lyon in France, it is often unearthed alongside malachite, a green copper pigment, although azurite itself

[96] Panayotova et al., *Colour*, p. 29.

sometimes appears green due to degradation of the hydroxycarbonate to carbonate. The mineral holds its colour when ground, making it an easy pigment to prepare - coarsely ground azurite is darker blue, and more finely ground azurite is lighter. High-grade azurite with homogeneous particle size and few impurities can be achieved through simple levigation, sieving, and grinding (although a greenish undertone from scattered particles of malachite and cuprite is expected - c.f. the purplish undertone of lapis lazuli). The ease of its excavation and preparation into a workable pigment means it was in use since antiquity, even more so because azurite is stable and unreactive in the atmosphere. Evidence of its use has been found in the Ancient Roman settlement of Cataractonium (Catterick) in England.[97]

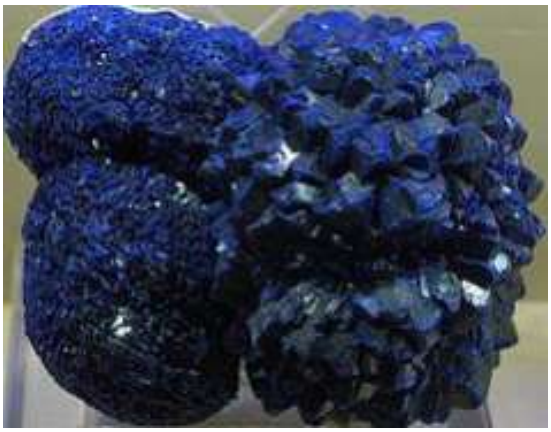

Figure 12: Azurite in its natural form.

These properties mean that azurite, although still expensive when compared to indigo, was a cheaper but worthy alternative to the much sought after, but more costly, lapis lazuli. Recent estimates suggest that in fourteenth- and fifteenth-century Britain, azurite was between ten and sixty times cheaper than lapis lazuli.[98] Deployed prolifically during this time in Britain, azurite was rarely employed much before the thirteenth century. The rarity of the pigment before the thirteenth century is in contrast with German-made manuscripts where tenth- and eleventh-century books see azurite routinely deployed, likely due to their proximity to the area where the mineral is found.[99] Azurite achieves parity with lapis lazuli in terms of the amounts employed in the mid thirteenth century in England, as seen in The de Brailes hours, examined at New College Oxford.

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[97] C Antink et al., *Contact, Concord and Conquest: Britons and Romans At Scotch Corner*, vol. 5 (Northern Archaeological Associates Monograph Series, 2020), p. 661.
[98] Richard Gameson et al., 'Late Medieval English Illuminators' Blues', (forthcoming). Please note that L. Garner is named on this paper.
[99] Gameson et al. Please note that L. Garner is named on this paper.

Azurite is stable and easily applied as paint, although it sometimes darkens when exposed to sulfur fumes. Whereas copper greens are notorious for their destruction of the parchment support over time, azurite-induced destruction is unusual - although occasionally strike-through of the pigment can be observed.

Azurite is optically dense, providing good coverage for blue areas and, as such, it was often deployed alone and was the pigment of choice for text ornamentation and flourishing. Occasionally azurite is deployed in ways expected of lapis lazuli, on the robes of Jesus, for example, even when lapis lazuli was used on the same page, and so was evidently available. A notable example of this is on the Fitzwilliam Museum's MS 40 fol. 44v, where Judas is coloured in lapis lazuli, yet Christ is painted with a mixture of azurite and lapis lazuli.[100] Sometimes lapis lazuli and azurite were combined in a mixture, or one was painted over the other to provide a different tone for shading. More commonly, the two were deployed close by, but in different zones of an illumination.

Azurite is primarily identified by two sharp bands in the NIR reflectance spectrum, at 2281 and 2350 nm, as seen in the sample spectrum in Figure 13.[101] It does yield a Raman spectrum, although the peaks quoted in recent literature (1095 and 835 cm^{-1} at 633 nm) were obtained with a laser power density of 2.63 mW μm^{-2}, which is considered too high for work on cultural artefacts. Team Pigment keeps laser power density at less than 0.5 mW μm^{-2}. Similarly, the peaks obtained under 532 nm excitation (at 400, 247 and 1096 cm^{-1}) were also obtained with a laser power density that is considered too high.[102]

[100] Panayotova et al., *Colour*, p. 39.
[101] John K. Delaney et al., 'Use of Imaging Spectroscopy, Fiber Optic Reflectance Spectroscopy, and X-Ray Fluorescence to Map and Identify Pigments in Illuminated Manuscripts', *Studies in Conservation* 59, no. 2 (March 2014), p. 97.
[102] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1223.

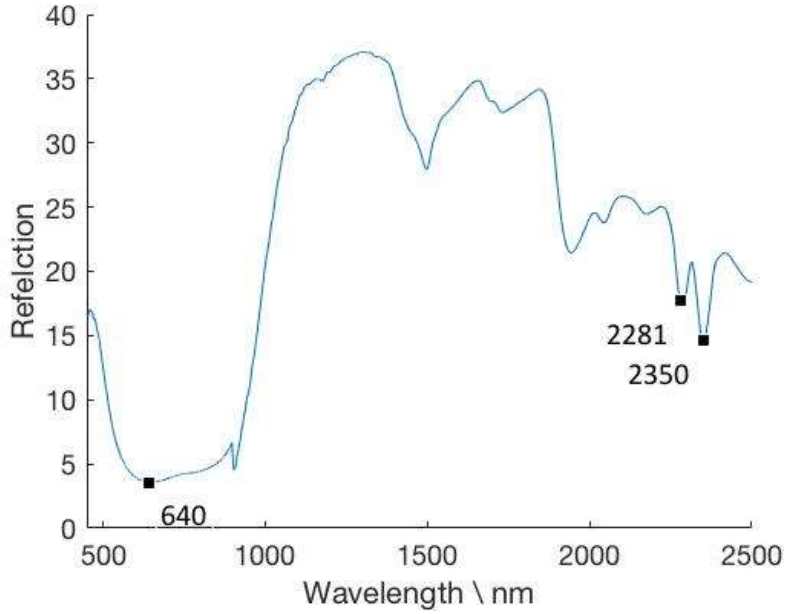

Figure 13: A laboratory sample spectra of levigated azurite obtained from rock.

Lapis lazuli, lapis ash and ultramarine

Lapis lazuli, thought of as the most exotic pigment as it came from across the sea, is extracted from a rock composed of a mixture of minerals, usually calcite, pyrite and lazurite. Seen in Figure 14, the pigment is sometimes called ultramarine ('beyond the sea'). However, ultramarine is now the name more frequently given to the synthetic version of the substance, which was first manufactured in the nineteenth century, with lapis ash being the name given to the remnants of the mineral after the lazurite pigment has been extracted from the crude lapis stone. Unless the mineral exhumed is exceptionally pure, simple grinding and washing renders the pigment a dull grey - to gain the vibrant colour from the stone involves a lengthy process, using a series of grinding, washing in wood ash lye, and capturing the blue colour with beeswax and resin.

Lapis lazuli and ultramarine share the same structure and chromophore, which is an S_3 radical anion 'trapped' into an $Al_6Si_6O_{24}$ cage structure. Lapis lazuli is most famously mined in the Badakhshan mines in the Kokcha River Valley, Afghanistan. Thus, its presence in a manuscript indicates that at the time of production there was a trade route directly from Persia.[103]

There are many contemporary recipes for extracting lapis lazuli from crude rock, or for synthesising blue pigments – The Montpellier *Liber diversarum arcium* offers approximately forty different notes

[103] Gameson et al., 'Late Medieval English Illuminators' Blues' (Please note L. Garner is named on this paper).

on ways to produce blue, under the heading, "On the preparation and purifying and washing of azure, and on getting its colour, and its tempering, and recognition excellence". However, within these instructions there is much confusion over the difference between 'azure', 'lapis lazuli', 'lazulum', and 'Armenian Stone' (likely azurite), amongst other blues termed 'blue verdigris' and 'Baghdad indigo'. It is clear that despite some of the recipes hinting at the parts of known methods for preparation mentioned above, in the *Liber diversarum arcium* at least, no foolproof procedure for extraction was circulating amongst its readers, perhaps indicating that lapis lazuli pigment extraction was more likely to have been performed 'off-site', maybe even at Badakhshan itself before the pigment was exported.

Vibrant blue lapis lazuli has been found in manuscripts in Britain from the tenth century, and in Carolingian Manuscripts in France from c. 800 CE.[104] This means that either the technology for the extraction of lapis lazuli from crude rock was around before this date, or the lapis lazuli deployed was extracted from sources with very few contaminants.

At times lapis lazuli was traded at a price comparable with gold and, when in high demand with limited supply, its price was up to sixty times more expensive than azurite, in many ways a comparable pigment.[105]

Figure 14: Lapis Lazuli in its natural form.

Lapis lazuli is primarily identified by its easily recognisable Raman spectrum with peaks at 545 and 1096 cm^{-1}. Further peaks, including those at 258 and 822 nm, can also be detected in a good sample, as seen in Figure 15. The pigment also gives a characteristic FORS spectrum with an absorbance

[104] Charlotte Denoël et al., 'Illuminating the Carolingian Era: New Discoveries as a Result of Scientific Analyses', *Heritage Science* 6, no. 1 (10 May 2018), p. 28.
[105] Gameson et al., 'Late Medieval English Illuminators' Blues'.

maximum at 600 nm, as seen in Figure 16, with reflectance in the red and NIR zones, which belies its reddish undertones (c.f. to the greenish undertones of azurite seen in its FORS spectra, where there is little reflectance in the red and NIR). There are no discernible features in the IR region of the spectra, unlike azurite.

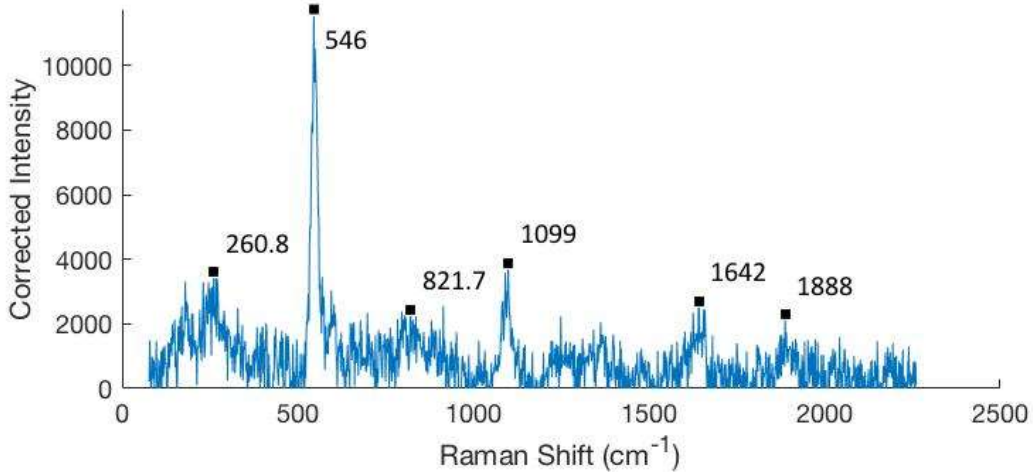

Figure 15: A sample Raman spectrum of lapis lazuli.

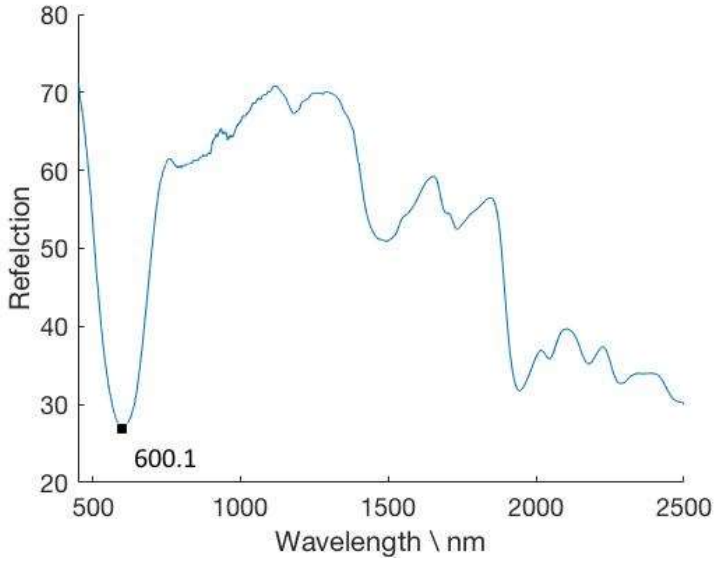

Figure 16: The FORS spectra of a laboratory sample of lapis lazuli.

Egyptian Blue

Egyptian blue ($CaCuSi_4O_{10}$) is an analogue to the rare, naturally occurring cuprorivaite. It is thought to be the first synthetic pigment of any colour and was manufactured by the Ancient Egyptians from sand, crushed limestone, natron and bronze or copper from around 2000 BCE. However, it seems that knowledge of how to make Egyptian blue was lost as it disappears from general use around the fourth century CE.[106] Egyptian blue is exceptionally fluorescent, and this property is therefore the best way to identify it. It has recently been detected in several manuscripts where it was previously assumed that the pigment was pure lapis lazuli. It makes surprising appearances in manuscripts in Canterbury in the tenth century and Carolingian manuscripts c.800.[107] This suggests that perhaps the expensive lapis lazuli was cut and extended with Egyptian blue somewhere along its trade route.[108]

There have also been small quantities of Egyptian blue found in other works: the Godescalc Gospel-lectionary (Paris, BnF MS Lat. 1203) that was made for Charlemagne from 781-3 BCE; a Winchester benedictional from the mid-tenth century (BnF, Lat. 987); and the Winchcombe Sacramentary (Orleans, Bibliotheque municipale MS 127) made in Southern England in the late tenth century.[109]

Smalt

Figure 17: Smalt, pre-ground.

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[106] Eastaugh, *The Pigment Compendium*, p. 153.
[107] Gameson, Beeby, and Nicholson, 'Colour at Canterbury', p. 25; Denoël et al., 'Illuminating the Carolingian Era', p. 1.
[108] Gameson, Beeby, and Nicholson, 'Colour at Canterbury', p. 25.
[109] Jean Vezin and Patricia Roger, 'Étude des matériaux de la couleur dans les manuscrits médiévaux : emploi inédit de bleu égyptien dans trois manuscrits des VIIIe et Xe siècles', *Comptes rendus des séances de l'Académie des Inscriptions et Belles-Lettres* 151, no. 1 (2007), p. 67.

Smalt, shown in Figure 17 in its state before being prepared for use as paint, is finely ground glass that contains cobalt, which provides the blue colouring. It is thought that the production of smalt was concentrated in Venice, which was a centre of glass manufacturing during the medieval period.[110]

As such, it is mainly found in later medieval Italian manuscripts, although has been identified in some English made manuscripts in the later fifteenth century - in the Spicer Hours, for example.[111] The exact chemical composition of smalt varies slightly depending on production but can be roughly described as SiO_2 (65%), K_2O (15%), Al_2O_3 (5%) and CoO (10%). According to Aceto et al. smalt can be identified by three bands in the 550-650 nm range, at 545, 600 and 640 nm, an example of which can be seen in Figure 18.[112]

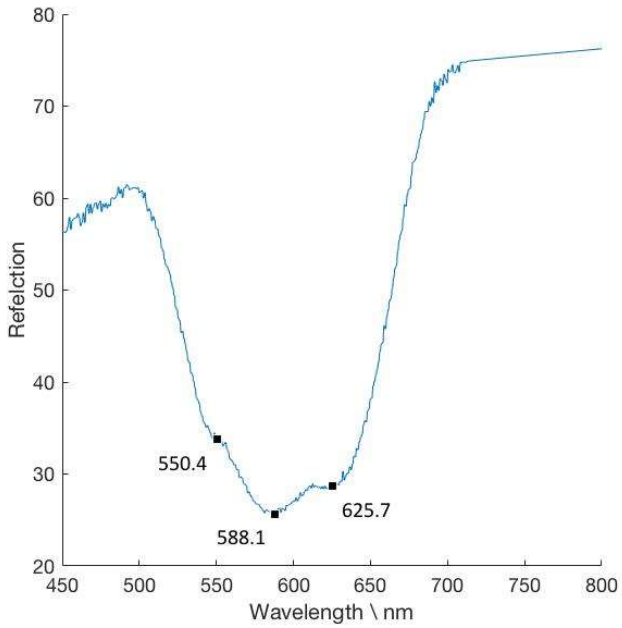

Figure 18: The FORS spectrum of a laboratory sample of smalt.

[110] Panayotova et al., *Colour*, p. 30.
[111] The Spicer Hours were examined whilst at Sam Fogg, an art dealership in London. I am unable to ascertain their current whereabouts.
[112] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

Indigo and Woad

Figure 19: An indigo plant, left, and a woad plant, right.

Deep blue indigo is obtained from (among other plants) *Indigofera tinctoria* or *Isatis tinctoria* (shown in Figure 19). Commonly known as indigo and woad, respectively, both yield a chemically identical product. The first is native to Africa and Asia, whilst the second is native to much of Britain and Europe. Some sources state that indigo for manuscripts was harvested from the indigo plant and imported from Baghdad in the fourteenth century. However, it is more likely that most of the pigment used in Western manuscripts was derived from European woad.[113] Certainly, it is found in manuscripts made well before the fourteenth century, such as the St. Augustine Gospels, which dates from 598 CE, and the Lindisfarne Gospels made c. 700 CE.[114]

Indigo ($C_{16}H_{10}N_2O_2$) can be extracted from either plant (the compounds obtained cannot be distinguished) and stored in solid form as a powder. This is, therefore, a rare example of an organic source yielding a pigment and thus is used as both a vat dye and a solid to make paint. Its chemical composition is very similar to that of Tyrian purple, as seen in Figure 20. As indigo is inert to oxidation, it has better lightfastness than other dyes but does not match that of azurite and lapis lazuli. This factor, combined with the fact that indigo was a common and cheaply obtained pigment, means that it is generally reserved for shading, making greens when combined with yellow, and for flourishing.

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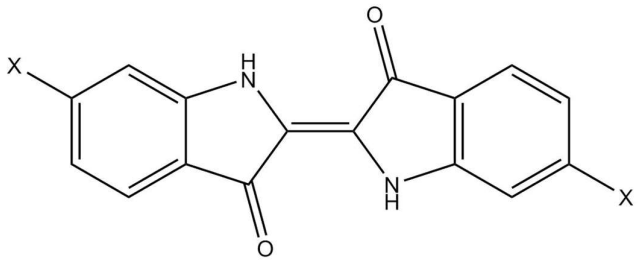
[113] Panayotova et al., *Colour*, p. 61.

[114] Gameson, Beeby, and Nicholson, 'Pigments of the Earliest Northumbrian Manuscripts', p. 58.



X=Br for Tyrian purple X=H for indigo

Figure 20: Molecular structure of indigo or Tyrian purple.

Indigo can be best identified in manuscripts from its Raman spectrum, with peaks at 1578 and 1325 cm^{-1} but also at 250 and 600 and 672 cm^{-1}, as seen in the lower wavelengths of the spectrum below. It also gives a weak fluorescence band when excited at 633 nm, which appears in the Raman spectrum with a peak that shifts depending on the density of the pigment due to inner filter effects, as can be seen in Figure 21. The FORS spectrum of indigo can be identified by its absorbance maxima at 660 nm, as seen in Figure 22. There are no distinguishing features in the NIR portion of the spectrum.

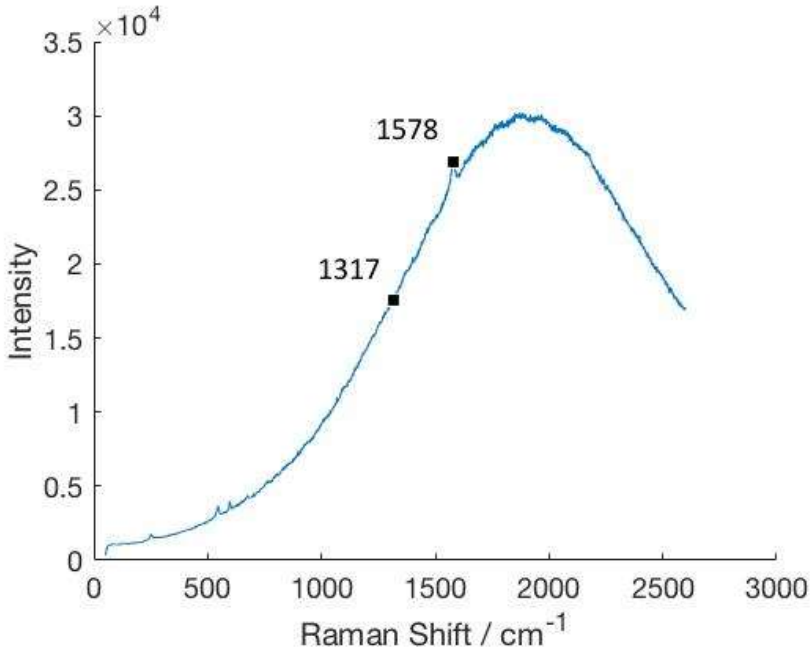


Figure 21: A laboratory sample Raman spectroscopy spectrum of indigo.

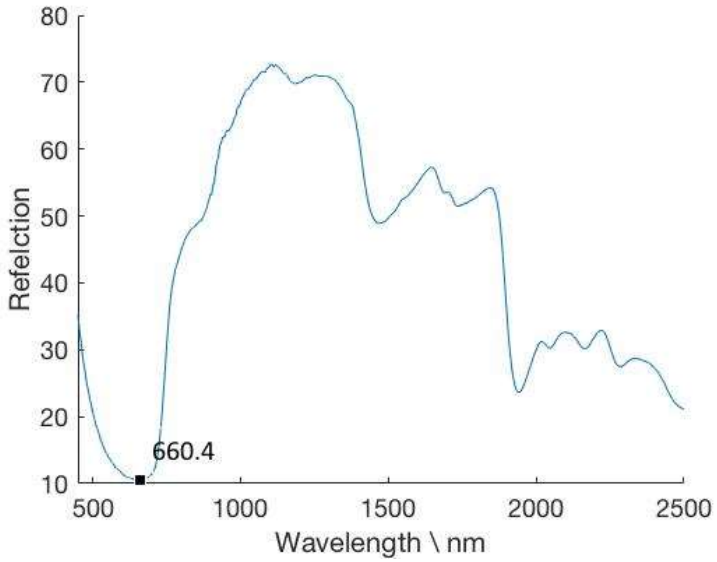


Figure 22: A FORS spectrum of a laboratory sample of indigo.

Green

Green can symbolise nature, new life, and hope and is sometimes associated with the Virgin Mary or with angels. To neutralise harsh skin tones, illuminators, and indeed artists working in other media, sometimes painted green underneath flesh colours (as detailed further in the section on verdigris, below).[115]

All the green mineral pigments contain copper, which were known, certainly in the later Middle Ages if not the earlier, to degrade the parchment support on which they sit, and therefore were used sparingly. The Durham Gospels, dating from c.700 CE, contains a copper green pigment that is eroding the writing support, as does the Book of Durrow (c. 650 – 700 CE) where the green has been identified as copper acetate.[116] Cennini wrote that green was 'beautiful to the eye, but it does not last'.[117] It has been reported that saffron has a 'significant preventative effect' on the degradation of copper pigments on the writing support in Persian and Indian works.[118]

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[115] Web Exhibits Website, 'Overview - Green Earth', accessed 6 November 2017, http://www.webexhibits.org/pigments/indiv/overview/greenearth.html.

[116] Google Arts & Culture, 'The Book of Durrow - The Library of Trinity College Dublin', accessed 21 December 2020, https://artsandculture.google.com/exhibit/the-book-of-durrow/tAKy0erUfMJQIQ.

[117] Panayotova et al., *Colour*, p. 31.

[118] M. Barkeshli and G. H. Ataie, 'PH Stability of Saffron Used in Verdigris as an Inhibitor in Persian Miniature Paintings', *Restaurator. International Journal for the Preservation of Library and Archival Material* 23, no. 3 (1 September 2002), p.154.

Greens in manuscripts are notoriously difficult to identify - whereas some recipe texts from the period indicate that only a few green pigments were used (*Liber diversarum arcium*, for example, mentions only verdigris) in actuality, many variations in composition exist.[119] In addition, as detailed below, Raman spectroscopy at the low powers required for safe study of manuscripts is not conducive to producing spectra.

Malachite

Malachite is a naturally occurring mineral ($Cu_2CO_3(OH)_2$) often found alongside azurite, and the pigment is prepared in much the same way. Although the source for the medieval supply of malachite has not been determined, it is likely to have come from deposits in Cornwall, Chessey in France, Hungary, Germany, or Greece and along the same trade routes as azurite.[120]

Malachite was fairly expensive in the Middle Ages. It was used as a pigment only rarely, perhaps as the stone is highly prized decoratively, but maybe also because it has a low refractive index - meaning that in some binders it does not produce the hiding power or opacity that an artist might crave.[121] When ground too finely the colour becomes very pale.[122] In France, there is some evidence that malachite was used only rarely before 1400, and that around this time malachite then becomes the pigment of choice, superseding verdigris.[123]

Malachite can be identified by its FORS spectra, which has absorption bands in the SWIR between 2200 and 2350 nm that are attributed to O-H and CO3 overtone and combination bands, and an absorbance maximum at 800 nm due to d-d ligand field transitions. However, the SWIR band can be difficult to observe. In Figure 23 the spectrum of a laboratory sample of malachite is shown. The absorbance maximum of 800 nm is clearly seen, but the band at 2277 nm could be the identifying absorption band, or could just be the absorption pattern seen in other NIR profiles (e.g. in Figure 22 above or in Figure 24 below). The most reliable and distinctive peaks in the identification of malachite by Raman Spectroscopy are at 440 and 1490 cm^{-1}. Other peaks may be visible, but their intensity changes depending on the orientation of the pigment particles,

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[119] Paola Ricciardi, Anuradha Pallipurath, and Kristine Rose, '"It's Not Easy Being Green": A Spectroscopic Study of Green Pigments Used in Illuminated Manuscripts', *Analytical Methods* 5, no. 16 (2013), p. 3820.
[120] Eastaugh, *The Pigment Compendium*, p. 254.
[121] Ball, *Bright Earth*, p. 128.
[122] Eastaugh, *The Pigment Compendium*, p. 254.
[123] Ricciardi, Pallipurath, and Rose, '"It's Not Easy Being Green"', p. 3823.

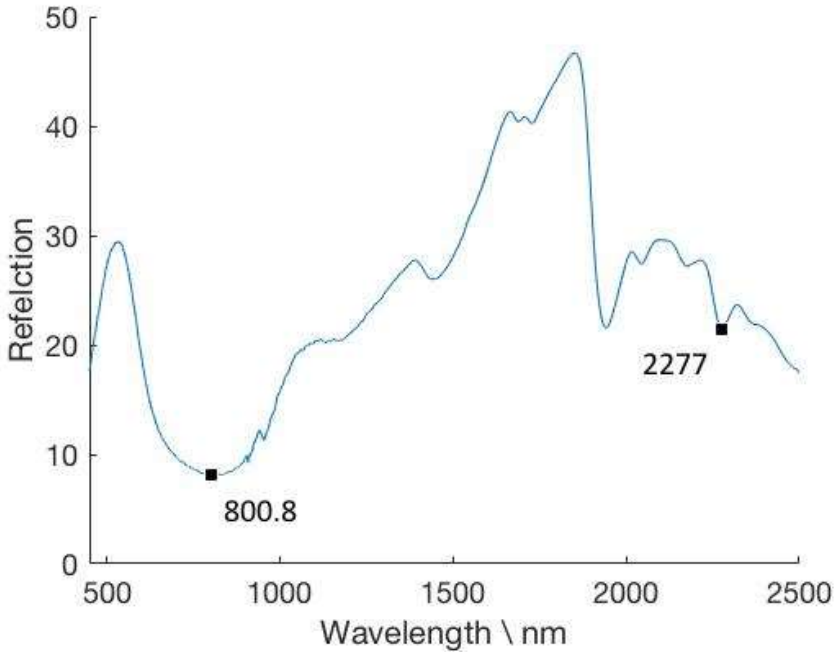

Figure 23: The FORS spectrum of a laboratory sample of malachite.

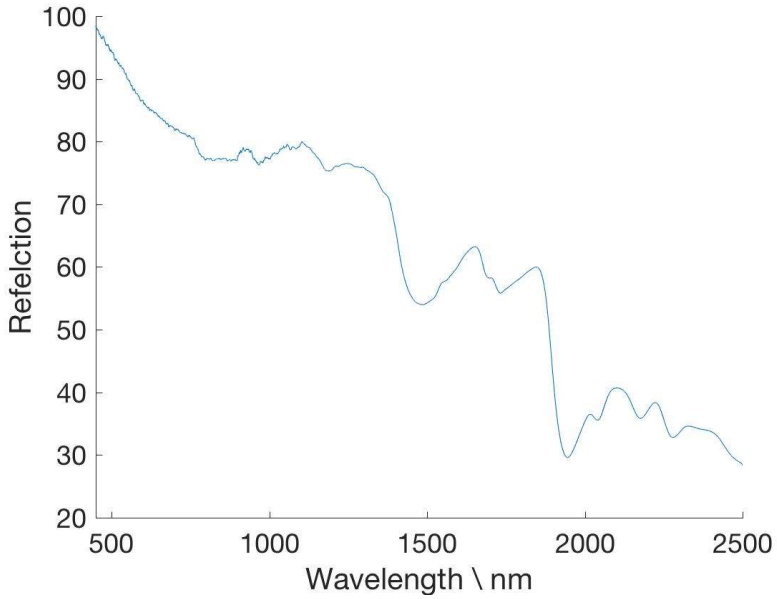

Figure 24: A FORS spectrum of a laboratory sample of blank cow parchment.

Malachite has been tentatively identified in manuscripts including the Manchester John Ryland's Library MS Lat. 24, which was made in Southern England in the thirteenth century, and in the tenth-

century manuscript Cambridge Trinity College B.11.2. However, as these identifications rely only on their FORS spectra, it would be presumptive to take them as diagnostic.[124] Confirmation of identification with another method, e.g. Raman spectroscopy, would be preferred and a sample spectrum can be seen in Figure 25. In the case of CTC B.11.2, no characteristic malachite spectrum was obtained, possibly due to the laser wavelength (633 nm was employed rather than 532 nm which is more suitable for green pigments) or because the power density of the laser was kept low (< 0.5 mW μm^{-2}) in order to ensure no damage occurred to the manuscripts examined.

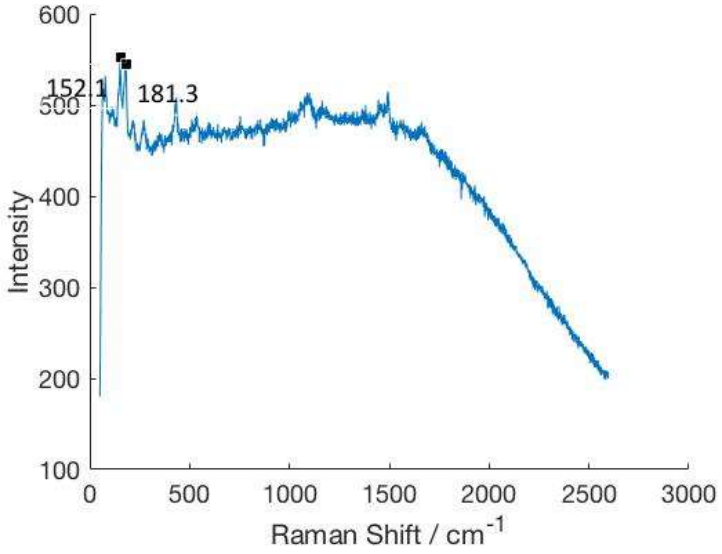

Figure 25: A laboratory sample Raman spectroscopy spectrum of malachite.

Verdigris

Also known as 'copper green', verdigris can be either applied as a 'catch-all' term for copper acetates, copper chlorides, copper carbonates and others, or it can be the term for a specific pigment.[125] This study uses the latter definition.

Verdigris (copper acetate) is produced by the natural weathering effect seen as the patina on copper and can be hastened by exposing the copper metal to a little acetic acid, or vinegar. Thus, the pigment is easily manufactured on a small scale, but larger workshops would probably have imported it.

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[124] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1488; Ricciardi, Pallipurath, and Rose, '"It's Not Easy Being Green"', p. 3820.

[125] Ricciardi, Pallipurath, and Rose, '"It's Not Easy Being Green"', p. 3820.

Montpellier was a centre for its manufacture in the Middle Ages.[126] Indeed, it has been described as "the pigment of choice" for illuminators in twelfth- and thirteenth-century France.[127]

Verdigris could be used alone or mixed with some other colours - Cennini describes a mixture of saffron and verdigris as making the 'most perfect grass colour'. However, he and the author of the Mappae Clavicula are keen to point out that verdigris is incompatible with many pigments, including orpiment. A recent study confirms that orpiment reacts with verdigris, causing the verdigris to darken where the pigments are in close proximity.[128]

Verdigris, like malachite, does have a Raman spectrum under 633 nm excitation (with peaks at 73 and 1438 cm^{-1}). However, this spectrum is very difficult to obtain using 633 nm excitation and laser power suitable for manuscript use (< 0.5 mW μm^{-2}).

Vergaut

Vergaut is created from a mixture of blue and yellow, most commonly indigo and orpiment, although sometimes lapis lazuli or azurite were employed for the blue component and lead-tin yellow, saffron or other organics for the yellow.[129] As the elements that make up a vergaut differ, there is no one identifying spectrum - instead a combination of spectra from the yellow and the blue colourants would be seen.

Organic Greens

Greens derived from plants and saps must have been commonly employed during the Middle Ages due to their ease of use and abundance in nature. Buckthorn (*Rhamnus cathartica)* berries have been tested in laboratory experiments and found to make a stable organic green known as sap green, which was stored in a pig's bladder or other receptacle.[130] These would have been harvested in the locale but, as they were also employed as a powerful laxative, they would have probably been available from

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[126] Panayotova et al., *Colour*, p. 63.

[127] Ricciardi, Pallipurath, and Rose, '"It's Not Easy Being Green"', p. 3823.

[128] Marc Vermeulen et al., 'The Darkening of Copper- or Lead-Based Pigments Explained by a Structural Modification of Natural Orpiment: A Spectroscopic and Electrochemical Study', *Journal of Analytical Atomic Spectrometry* 32, no. 7 (2017), p. 1331.

[129] Ricciardi, Pallipurath, and Rose, '"It's Not Easy Being Green"', p. 3821.

[130] Claire Siconolfi, 'Sap Green from Buckthorn Berries (Part 1)', accessed 26 October 2017, http://medieval-whimsies.blogspot.com/2013/09/sap-green-from-buckthorn-berries-part-1.html; Panayotova et al., *Colour*, p. 34.

the local apothecary.[131] Iris green was concocted from the blue and green iris flowers *Iris germanica*, from which Thompson asserts a green lake can be made.[132]

Sap green and iris green both have absorbance maxima around 605 nm when examined with FORS.[133]

Green Earth

Also known as terre verte or Verona green, green earth is derived from mineral sources in the ground and, as such, has been used since antiquity. Green earth is a mixture of minerals, mainly glauconite, or mainly celadonite (the two are never found together), with chlorite and other minerals. It can be mined in Bohemia, Poland, and France although the most famous terre verte was mined at Monte Baldo, Verona, giving the colour its alternative name. Particularly pertinent to this study is the fact that the mineral can be mined in both France and the Mendips in Southern England.[134]

The pigment is a permanent, stable, and unreactive one, prepared by washing, grinding, and handpicking to remove impurities, and then perhaps levigation to remove any remaining impurities. It was often used in medieval tempera paintings under flesh tones, to balance out the red and pink applied on top, as to apply pinks and reds to the gesso beneath would give a sunburnt quality to the faces and skin. Where the flesh colours have faded the green colour beneath remains, as green earth is a lightfast pigment and is unaffected by other pigments, although it has low hiding power.[135]

It has tentatively been identified in an Icelandic manuscript c.1360 (Reyjavik, Skarðsbók, Codex Scardensis AM 350) by a strong absorption band at 410 nm when examined by diffuse reflectance spectroscopy.[136]

Purple

Purple is a colour associated with wealth and royalty; the Roman Emperors certainly regarded purple as their colour of choice, and its use was closely guarded in Ancient Rome, and later in Europe, by sumptuary laws. Aside from the dyes examined below, which are all organic, purple can, of course, be

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[131] Panayotova et al., *Colour*, p. 63.

[132] Josefin, 'Iris Green', *Silwa Goes Purjo* (blog), 25 June 2018, https://silwagoespurjo.com/2018/06/25/iris-green/.

[133] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

[134] Eastaugh, *The Pigment Compendium*, p. 181.

[135] Web Exhibits Website, 'Overview - Green Earth'.

[136] Stephen P. Best et al., 'Identification by Raman Microscopy and Visible Reflectance Spectroscopy of Pigments on an Icelandic Manuscript', *Studies in Conservation* 40, no. 1 (February 1995), p. 31.

realised by combining red and blue pigments, although in practice this is rarely seen. There are a few manuscripts, such as MS McClean 30 at the Fitzwilliam Museum, Cambridge, that have purple parchment, and are written in silver or gold ink.

Folium

Folium is obtained from the seeds of the fruit of the turnsole plant (*Chrozophora tinctoria)* also known as solsequium, as the plant is heliotropic. The plant is native to the Mediterranean area, and thus folium dye would have been exported from the region on clothlets. Detailed instructions on the extraction of the dye are given in *Montpellier liber diversarum arcium* and *on divers arts,* which both report the dye as being pH-sensitive and thus able to be red, blue, or purple (folium rubeum, folium saphireum, and folium purpureum).[137] This fact is repeated in contemporary literature.[138]

However, this pH dependant property is disputed by Aceto et al. who claim that the different colours of folium come, in fact, from the maturation state of cuticles of the plant – a blue colour coming from unripe fruit, and a purple coming from ripe fruit – the fabled red folium being contamination with iron.[139] Further experiments by Aceto et al. have shown that the identifying features of the folium FORS spectrum are unchanged in the pH range 3-10, which does indeed suggest that the colour is not pH-dependent.[140] In my own experiments in the laboratory at Durham University, I have never been able to observe a colour change when a solution of folium and water were subjected to differing pH.

The structure of the chromophore of folium has recently been identified and named as chrozophoridin, its colour yielding an absorbance maximum of 540 nm, due to a HOMO-LUMO transition.[141] This is at odds with previously published works, which identify folium as having two absorbance maxima at 545 nm and 580 nm.[142] Folium is a dye, its spectral features are liable to change with the method of preparation and the substrate employed if it is made into a lake.[143] Like other lake pigments, folium is not lightfast as a dye or solid. Folium has been identified as the colourant in a sixth-

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[137] Theophilus, *On Divers Arts*; Clarke, *Mediaeval Painters' Materials and Techniques*, p. 180.
[138] Panayotova et al., *Colour*, p. 30.
[139] M. Aceto et al., 'The Quest for Folium. Proceedings of DHA34 - Dyes in History & Archaeology 34 Conference, Thessaloniki', 2015, p. 36.
[140] Maurizio Aceto et al., 'On the Identification of Folium and Orchil on Illuminated Manuscripts' 171 (January 2017), p. 463.
[141] P. Nabais et al., 'A 1000-Year-Old Mystery Solved: Unlocking the Molecular Structure for the Medieval Blue from *Chrozophora Tinctoria*, Also Known as Folium', *Science Advances* 6, no. 16 (April 2020), p. 5.
[142] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.
[143] Aceto et al., 'On the Identification of Folium and Orchil on Illuminated Manuscripts', p. 466.

century purple-dyed manuscript fragment, the Sinope Gospels (Paris, BnF, MS gr. 1286, also known as the Codex Sinopensis). [144] A detailed examination of the folium FORS spectrum can be found in chapter four, where it is tentatively identified in a manuscript.

Orcein

Orcein is obtained from lichens, such as *Roccella tinctoria* and other genera, and is extracted by fermentation in ammonia (urine). The dye is pH dependant and can yield colours from orange to red to blue. Orcein is primarily identified by its FORS spectrum, which, like folium, shows a double absorbance maximum at around 550 and 590 nm.[145] Orcein also yields a Raman spectrum with peaks at 1644 and 1518 cm^{-1}, as seen in Figure 26, although at low laser power density this can be difficult to obtain.[146] Aceto et al. have discovered orcein used to colour parchment in manuscripts from the sixth century, such as the Gothic masterpiece *Codex Argenteus,* a book written in silver ink on purple parchment (Uppsala Universitetsbibliotheket DG.1).[147]

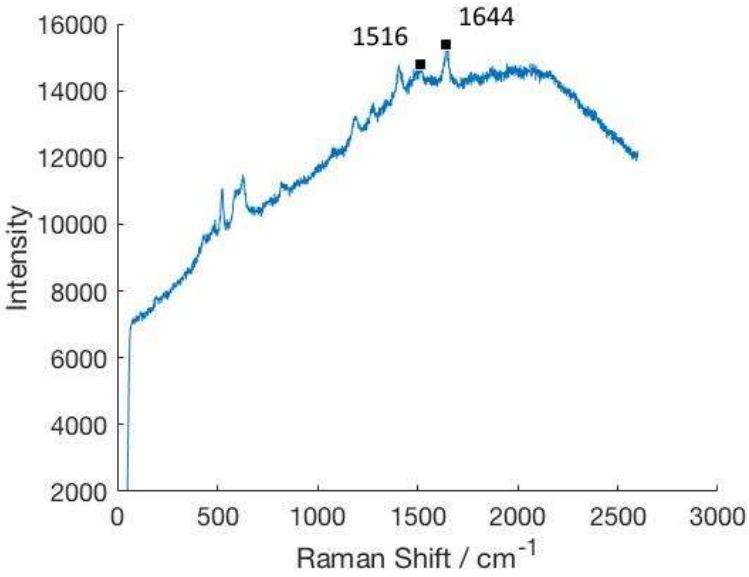

Figure 26: A laboratory sample Raman spectroscopy spectrum of orcein.

[144] Clarke, *Mediaeval Painters' Materials and Techniques*, p. 180.
[145] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.
[146] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.
[147] Aceto et al., 'On the Identification of Folium and Orchil on Illuminated Manuscripts', p. 467.

Tyrian

Also known as Royal or Imperial Purple, Tyrian purple is famed for its value and robust colour and was a highly prized dye. Extracted from glands of the sea snails *Murex* and *Purpura* from the *Muricidae* family, its name is thought to be derived from its place of manufacture – Tyre in Lebanon. Its chemical structure, seen in Figure 20, is very close to that of indigo - containing bromine instead of hydrogen - and is now able to be synthesised.

The fact that bromine is in the molecule has, in the past, led to some false identifications of the pigment in manuscripts. The X-ray Fluorescence technique (known as XRF and explained in detail in Chapter Three) can identify traces of bromine, and thus upon examining some purples in manuscripts, its presence led researchers to believe that Tyrian purple was present. However, subsequent research in 2013 showed that lichens growing near the coast, which can be processed to produce orcein, can contain bromine, as well as the plant that folium derives from – meaning that any purple colour in a manuscript has a strong chance of containing bromine and accordingly meaning that the presence of bromine does not automatically mean that the colour is Tyrian purple.[148] Thus, these identifications have been revised, and thus the colourant has yet to be identified in manuscripts.[149]

Black

Employed frequently in manuscripts to outline artwork, black was also employed as an infill where demanded by a scene. Often black was a modifier, darkening other colours – it was either included in the paint mixture, or applied over or under the paint as shading, dotting, or hatching.

Ink

Two types of ink have been identified in medieval manuscripts. One is carbon-based - a mixture of carbon (from soot or similar), gum and water. This ink has been in use since antiquity but has the disadvantage of occasionally scaling off the writing support. From around the third century, iron gall ink was employed, produced by extracting the tannins found in wood galls, in Britain usually oak galls, and mixing it with ferrous sulfate, gum Arabic, and water or wine. Iron gall ink has the advantage, and disadvantage, of being slightly acidic. Words written with it "eat" into the parchment page, which can

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[148] Cheryl Porter et al., 'Looking for Lichen, Fooled by Folium and Tricked by Tyrian: A Brief Tour and New Research on Purple in Manuscripts', in *Manuscripts in the Making: Volume Two* (Harvey Miller, 2017), p. 68.
[149] Panayotova et al., *Colour*, p. 18.

produce a longer-lasting more indelible result but can ruin the membrane if the mixture is too acidic. Carbon was sometimes added to oak gall ink to darken it.

Carbon Black

Black used for illustration, rather than for ink (as discussed above) was generally carbon-based. Either lamp black, where soot was collected from burning oil lamps or candles, or, less commonly, bone black or even ivory black, where the black charcoal formed after roasting animal bones, or ivory, would have been collected. It is highly likely that these carbon blacks would have been produced or sourced locally to any workshop, as they are by-products of processes that would have been occurring almost daily, i.e. the burning of candles for light and wood for fire.

Carbon can be detected informally by the fact that it absorbs all wavelengths from the UV to the mid-IR and hence appears dark under near-infrared wavelengths. Confirmation that the pigment is employed can be by Raman spectroscopy, where peaks of 1324 and 1594 cm^{-1} can be obtained, as seen in Figure 27, although their exact position can lie within a range, and their profile can depend on the degree of crystallinity. In the FORS spectrum, where carbon black shows absorbance across visible and NIR wavelengths, as seen in Figure 28.[150]

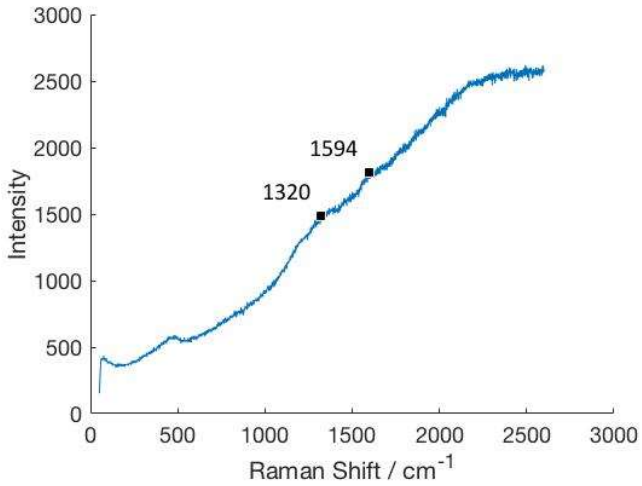

Figure 27: A laboratory sample Raman spectroscopy spectrum of carbon.

[150] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491; Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p.1222.

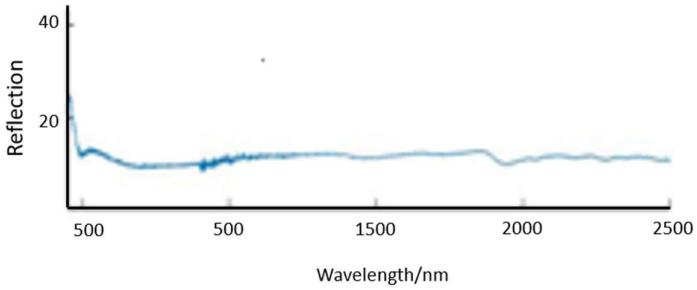

Figure 28: A laboratory sample FORS spectrum of carbon.

Antimony

In rare cases, a black antimony compound sometimes referred to as stibnite, has been seen employed in illuminations, although it can appear more grey than black on parchment.[151] Stibnite is found worldwide alongside metal deposits, in places such as Cornwall in England, as well as Saxony (Germany), and Attica (Greece), amongst others.[152] Due to its discovery in a German altarpiece dating from 1490 and a few manuscripts from c.1500, it is clear there was a trade in antimony around this time.

White

White could be a symbol of truth and purity, as the unadulterated colour would have been a rare sight in the Middle Ages, or a symbol of death, as the representation of deathly white bodies in shrouds attests.[153]

Naturally occurring whites derived from calcic sources such as chalk, eggshell or seashells would have been easily manufactured and would have been available in the locale, with bone ash from calcined animal bones also available as a cheap extender or substrate.[154]

White Lead

A more prestigious white, which was durable and easy to work with, was white lead - lead II carbonate ($PbCO_3$) or lead carbonate hydroxide ($2PbCO_3.Pb(OH)_2$). Although it occurs naturally as cerussite or hydrocerussite, there is scant evidence to show that this pigment was ever sourced from the earth; it

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[151] Panayotova et al., *Colour*, p. 35.
[152] Eastaugh, *The Pigment Compendium*, p. 359.
[153] Heather Pulliam, 'COLOR', *Studies in Iconography* 33 (2012): 3–14.
[154] Eastaugh, *The Pigment Compendium*, p. 98.

has been easily manufactured since antiquity. Vitruvius in the first century CE and Pliny in 77 BCE, amongst others, wrote on the subject. The *Mappae Clavicula* also details how to make ceruse (white lead) easily.[155]

Production entailed placing strips of lead metal in an environment rich in acetic and carbonic acid, and scraping off the precipitate which accumulated on the metal over a period of weeks. Such an environment could be easily created by placing strips of lead in pots of vinegar (acetic acid) surrounded by manure to produce water and carbon dioxide in the atmosphere along with warmth to expedite the process.[156] The precipitate (lead acetate) was then roasted in the air (oxygen) to produce white lead, or roasted for longer to produce red lead, which is described above.

White lead is best identified from its Raman spectrum, which has peaks at 70, 104, and 1050 cm $^{-1,}$ under a 633 nm laser, as seen in Figure 29, confirmed by a FORS spectrum with a band in the NIR at 1447 nm, as seen in Figure 30.[157] It is ubiquitous in artwork in manuscripts; Team Pigment have found white lead in manuscripts dating from the seventh century through to the eighteenth century.[158] However, despite its common deployment, it can be difficult to identify as the Raman bands can be quite weak and are easily swamped with fluorescence. Many Raman spectrometers do not operate at low wavenumbers and do not detect the bands at 70 and 104 cm^{-1}. XRF can detect the presence of lead but cannot identify its specific chemical form.

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[155] Fitzwilliam Museum Website, 'Lead White | ILLUMINATED', accessed 31 October 2017, http://www.fitzmuseum.cam.ac.uk/illuminated/lab/overview-of-artists-materials/lead-white/type/material.

[156] Eastaugh, *The Pigment Compendium*, p. 239.

[157] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts' p. 1222; Delaney et al., 'Use of Imaging Spectroscopy, Fiber Optic Reflectance Spectroscopy, and X-Ray Fluorescence to Map and Identify Pigments in Illuminated Manuscripts', p. 97.

[158] Gameson, Beeby, and Nicholson, 'Pigments of the Earliest Northumbrian Manuscripts', pp. 33-59; R. Mulholland et al., 'Identifying Eighteenth Century Pigments at the Bodleian Library Using in Situ Raman Spectroscopy, XRF and Hyperspectral Imaging', *Heritage Science* 5, no. 1 (18 October 2017), p. 9.

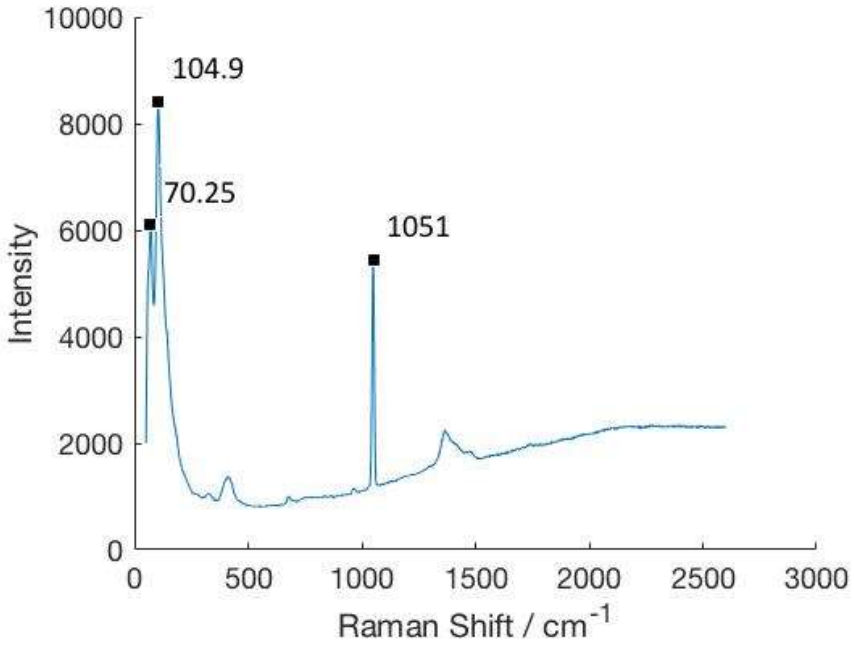

Figure 29: A laboratory sample Raman spectroscopy spectrum of white lead.

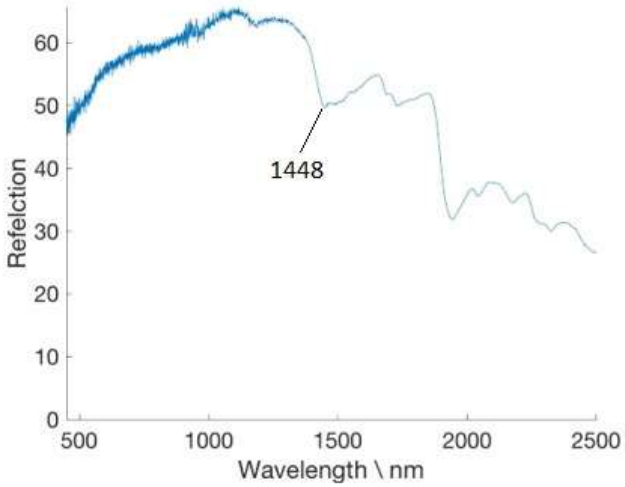

Figure 30: A laboratory sample FORS spectrum of white lead.

Chalk

A type of limestone, chalk ($CaCO_3$) is a very fine-grained, soft pigment and is both abundant and easily obtained and processed, needing only crushing and levigation to obtain a workable pigment, and for this reason, it is likely to have been used in the medieval palette. However, its properties also mean that it is relatively transparent in most paint binders and is therefore found more as an extender to

add a lighter tone or a base preparation for other pigments rather than the main pigment in its own right.[159]

Chalk is occasionally identified in manuscripts by its Raman spectrum with peaks at 154 and 278 cm^{-1} under 532 nm excitation. However, these findings are usually related to the preparation of the parchment for writing, as an addition to pink colourants, or as part of a bole underneath gold leaf.[160]

Brown

Ochre

In essence, ochres are clay-based minerals dug from the earth. As detailed above, they come in a variety of colours ranging from yellow to brown and red, but are sometimes even green or purple. Yellow ochre and some brown ochres are left unprocessed, save for washing and grinding, but brown-red ochre may be roasted, causing the iron oxide in the mineral to lose hydration, changing the colour. Ochres can be identified by their Raman spectra, depending on the colour. However, as ochre is only a moderately efficient scatterer, obtaining a spectrum when there is a fluorescent background or binder present can be challenging. FORS identification shows an interesting 'bump' in the reflectance spectrum, as seen above in Figure 8, the iron oxide spectrum. XRF can reveal the presence of iron in red ochre (red ochres are described in more detail above).

Metals

Metals used in illuminations would generally have been burnished, producing a shine, and so would have been thought to embody light itself – hence the word 'illumination'. Gold and silver were staple metals but other metals - copper, tin, and bronze - were sometimes employed.

Gold and Silver Leaf

Gold and silver could be beaten until they were a thin 'leaf' and delicately placed on top of a prepared mound of pigment and then burnished. The raised surface of the page enabled the metal to catch the light and to gleam, and if chosen well, enhanced the colour of the surface metal as well as providing a suitable background should the metal scale off. Pigments used in this way include orpiment, Armenian Bole, and red lead mixtures.

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[159] Eastaugh, *The Pigment Compendium*, p.98.
[160] Panayotova et al., *Colour*, p.36.

Coins were one source of gold and silver that could be beaten into leaf, by a process that has changed little since antiquity. Small gold pieces were placed in sheepskins and then hammered until the leaves were about 0.001 mm thick. One 5 mm nugget could be hammered out to cover about 0.5 m^2.[161] Cennini recommended that 100 leaves and no more, could be beaten from a ducket.[162]

Gold, silver, and other metals are best examined by XRF.

Shell gold and silver

Shell gold, or shell silver, was an alternative to leaf and would have given the artist more flexibility to shade, colour and over paint. So-called due to its final preparation and storage place of a sea-shell, shell metal was prepared by grinding the leaf metal with water and a suitable binder - modern methods use gum Arabic or honey, as both dissolve and can be washed away in hot water. Shell metals often appear granular under a microscope and so can be distinguished from leaf, although in some cases identification can be difficult.

Mosaic Gold

Mosaic gold is tin sulfide (SnS_2) and can be prepared by melting equal parts of tin, mercury, sulfur and ammonium chloride. Experiments to synthesise the pigment in the laboratory in Durham produced a compound that was very shiny and resembled pyrite (fool's gold) when first manufactured. However, the gleam and lustre of the pigment do not transfer to the page when the pigment is made into paint, which is often mustard coloured. Despite this, mosaic gold was often used as a substitute for gold metal in manuscripts. Cennini certainly knew of the pigment, as he commented that it was deployed more in manuscripts than for panel painting.[163]

Mosaic gold is identified by its Raman spectrum, with a strong peak at 310 cm^{-1}, as seen in Figure 31.[164] Its FORS spectrum gives an inflection point at 530 nm.[165] It is found regularly in fifteenth-century

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[161] Britanica.com, 'Gold Leaf', accessed 19 August 2019, https://www.britannica.com/art/gold-leaf.

[162] Panayotova et al., *Colour*, p. 65.

[163] Eastaugh, *The Pigment Compendium*, p. 274.

[164] Tracey D. Chaplin et al., 'Pigment Analysis by Raman Microscopy and Portable X-Ray Fluorescence (PXRF) of Thirteenth to Fourteenth Century Illuminations and Cuttings from Bologna', *Philosophical Transactions. Series A, Mathematical, Physical, and Engineering Sciences* 374, no. 2082 (13 December 2016), p. 11.

[165] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

manuscripts and has been identified in some Bolognese manuscript cuttings from the fourteenth century.[166]

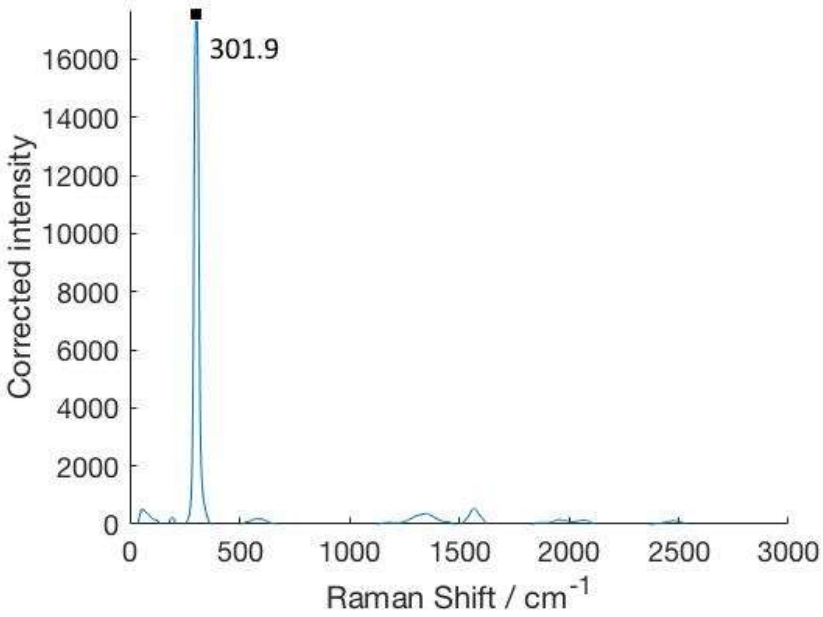

Figure 31: A sample laboratory Raman spectroscopy spectrum of mosaic gold.

Modern Pigments

As science and technology have advanced, so, of course, has the knowledge of how to synthesise pigments. To describe every modern pigment would be an enormous undertaking – new pigments are invented almost daily. However, described below are some modern pigments that are sometimes found in medieval manuscripts – the result of pre-modern conservation work or even forgery. As work on the analysis of pigments increases, and the knowledge of the science and technology available in the Middle Ages increases, it is likely that earlier and earlier deployment of these pigments, particularly bice and verditer, will be seen.

Titanium Oxide

Also known as titanium (IV) oxide or titanium dioxide, TiO_2 known as titanium white when used as in paint is a brilliant white pigment that is very similar to white lead but with the advantage of not being toxic. It is generally sourced from the naturally occurring ores of rutile, ilmenite and anatase, and was

[166] Chaplin et al., 'Pigment Analysis by Raman Microscopy and Portable X-Ray Fluorescence (PXRF) of Thirteenth to Fourteenth Century Illuminations and Cuttings from Bologna', p. 9.

first mass-produced in 1916. It is identified by its Raman spectrum with peaks at 143, 238, 450, and 615cm^{-1} under 633nm excitation.[167]

Prussian Blue

This blue pigment is an iron compound and was first synthesised in 1704, as the result of an accidental tainting of potash with animal waste. Since its inception, it has been widely used as a stable bright blue. It has Raman peaks at 276, 538, 956 and 2157 cm^{-1} under 633 nm excitation.[168]

Verditer and Bice

Verditer, sometimes referred to as bice, is the synthetic version of azurite. It can come in green or blue varieties depending on the method of manufacture. Usually, it is a mixture of copper carbonate and copper hydroxide and can be synthesised from copper nitrate and chalk. It can be distinguished under the microscope by the uniformity in size and shape of the particles manufactured, rather than the irregularity in size and shape of natural azurite particles.[169]

Bice, from the French work *bis*, originally meaning dark-coloured, is seen in medieval sources to refer to lower grade blues, compared to higher grade blues which were termed 'azur'.

Carmine (cochineal)

Cochineal from the Americas took over as the imported insect red of choice from the 1520s.

Ultramarine

Synthetic ultramarine is created relatively cheaply by using kaolin, a feldspar mineral, sulfur, anhydrous sodium carbonate and a reducing agent, such as oil. However, the process is not straightforward and necessitates many different stages, along with high temperatures.[170]

Ultramarine has been widely used for the restoration of blue in manuscripts. Synthesised ultramarine can be differentiated from natural lapis lazuli by chemometric analysis of FORS spectra, although this

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[167] M.C. Caggiani, A. Cosentino, and A. Mangone, 'Pigments Checker Version 3.0, a Handy Set for Conservation Scientists: A Free Online Raman Spectra Database', *Microchemical Journal* 129 (November 2016), p. 126.
[168] Caggiani, Cosentino, and Mangone, p. 126.
[169] Peter MacTaggart and Ann MacTaggart, 'Refiners' Verditers', *Studies in Conservation* 25, no. 1 (1980): 37–45.
[170] Eastaugh, *The Pigment Compendium*, p. 382.

can be time-consuming.[171] Alternatively, the two can be distinguished by features in a Raman spectrum observed between 1100 and 3300 cm^{-1} under 785 nm excitation. The peaks detected are thought to indicate the presence of the mineral diopside, whose presence in lapis lazuli confirms it as being of natural origin. Further investigation on the presence of this mineral may also allow differentiation between lapis lazuli mined in Afghanistan, and that mined in Chile.[172]

Conclusion

This chapter has detailed methods of manuscript manufacture with particular emphasis on the practises common in thirteenth-century Paris as this is the time and place that is the particular focus of this study. An overview of the texts that contained recipes and tips for pigment or dye procurement or manufacture has been provided, along with a brief explanation of the provenance of the material contained within them. This provides an overview and a context for the artistic practices, knowledge and know-how that was circulating in Northern France and Southern England at that juncture and, gives a sense of the artistic milieu in which the artists, scribes and illuminators were working when the manuscripts in this study were produced.

Furthermore, this chapter gives a comprehensive list of the typical and atypical pigments and dyes that were used in medieval book illumination. From this discussion, it is, therefore, possible to hypothesise which colourants might reasonably be expected to be found in manuscripts made in thirteenth-century France or England, which pigments or dyes that it would be unusual to find, and which would be extremely unlikely, or even impossible at the date and time in question. From this chapter, we can conclude that we are likely to see lapis lazuli, red and white lead, and carbon, amongst others, but we can be certain that, barring a forgery, we will not see Prussian Blue, for example.

As such, this chapter gives a foundation on which scientific analysis of colourants in thirteenth-century manuscripts, the techniques of which are detailed in the next chapter, can be performed.

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[171] Maurizio Aceto et al., 'Non-Invasive Differentiation between Natural and Synthetic Ultramarine Blue Pigments by Means of 250–900 Nm FORS Analysis', *Analytical Methods* 5 (21 August 2013): 4184, p. 4184.

[172] Catherine M. Schmidt, Marc S. Walton, and Karen Trentelman, 'Characterization of *Lapis Lazuli* Pigments Using a Multitechnique Analytical Approach: Implications for Identification and Geological Provenancing', *Analytical Chemistry* 81, no. 20 (15 October 2009), p. 8518.

Chapter Three

Spectroscopic Techniques in Pigment Identification

Introduction

As previously discussed, it is imperative that any identification and analytical work conducted on manuscripts be non-invasive and non-damaging. To this end, the field of spectroscopy - the study of how light interacts with matter - has been employed to great effect. This section details the theory, systems and techniques that are used by the Durham University based team for the examination of manuscripts *in-situ*, alongside laboratory-based systems and techniques that help to inform best practice and theory. Relevant laboratory experiments are described.

Fibre Optic Reflectance System (FORS)

Theory

Specular reflection is when light is reflected off a surface acting as a mirror. However, when light falls onto a matt surface, such as a patch of pigment on a manuscript, some wavelengths of light are absorbed by molecules at the surface, some are scattered internally and re-emitted from the surface, and some are reflected. This is known as diffuse reflection and is exemplified in Figure 1.

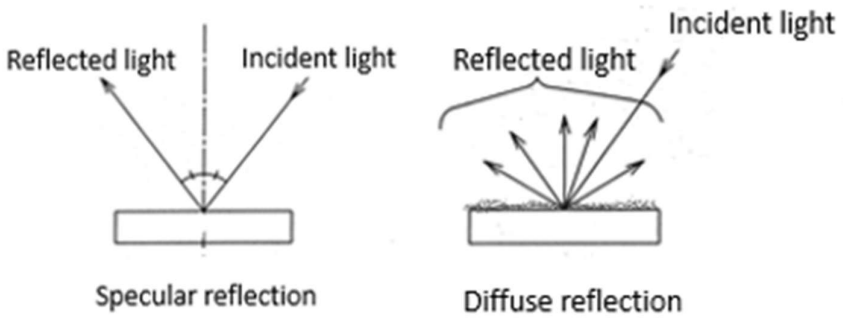

Figure 1: Diagram of specular and diffuse reflection.

This diffuse reflectance can be collected by a simple spectrometer, the details of which are given below, and reported as a ratio of relative reflectance compared to a white object that is taken to be of 100 % reflectance. The percentage reflectance *R*(%) is recorded with respect to wavelength (λ)

and is represented in Equation 1 below, where I_r is the measured reflectance, and I_o is the reflectance of the reference sample. Usually measured in W, the actual units of I_r and I_o are irrelevant as reflectance (R) has no units and is expressed as a fraction or a percentage.

$$\boldsymbol{R(\lambda) = \frac{Ir}{Io}}$$

Equation 1

When plotted, this gives a diffuse reflectance spectrum unique to the pigment in question. The identification of spectral features in the visible and near infrared wavelengths (approx. 400 - 2500 nm) such as absorbance maxima or minima, absorption bands or inflection points, can aid identification. Similarly, comparison of spectra between different pigments, and to a library of pigment spectra, is a helpful way of determining a pigment.

Limitations and Solutions of Diffuse Reflection

Although Diffuse Reflectance Spectra (DRS) can help identify organic dyes that might otherwise fluoresce (rendering other techniques such as XRF and Raman spectroscopy less useful), identifying dyes can be fraught with difficulties. Organic substances used as dyes can be produced as a juice or a lake (more details on these are given in Chapter Two). Both juices and lakes have various permutations depending on the extraction process, the substrate and/or the mordant used. Spectral features of a dye (or a pigment) can change with the addition of other colourants, even a white one. This, coupled with the low hiding power or opacity of some dyes (allowing the spectral signature of the writing support to be seen through the colourant) makes a comprehensive DRS determination extremely difficult.[1]

When used in conjunction with other techniques such as Raman, NIR reflectance and XRF techniques, DRS can be a powerful tool. It can help determine substances that do not respond well to other analysis due to their fluorescence. However, the spectra of some pigment samples can look very similar to each other, and spectral features can sometimes be broad and featureless, and so care must be taken when using DRS alone. Absorption features, whose wavelengths remain more constant despite the addition of other colourants, is one feature that can be key to identification.

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[1] Maurizio Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', *Analytical Methods* 6, no. 5 (2014), p. 1488.

One way in which the diffuse nature of such a reflectance spectrum can be mitigated to some extent is by mathematical transformation of the spectra. The Kubelka-Munk (K-M) theory considers the absorption and scattering of light in a sample beyond the surface layer. Light is assumed to be diffuse in all directions after penetrating the sample, although only the two net fluxes of vertically up and down are described.[2] The equation can be used to obtain two useful parameters, *k* and *s*, as seen in Equation 2, where *R* is the reflectance of the sample, *k* is the molar absorption coefficient, and *s* is the scattering coefficient.

$$f(R) = \frac{(1-R)^2}{2R} = \frac{k}{s}$$

Equation 2

The second derivative of the diffuse reflectance spectrum itself can also be used to provide quantitative information about a pigment. This can be especially helpful in determining concentrations of a sample – peaks and troughs of the raw data taken at different wavelengths are made more apparent and can be fitted to a function. The equation of this curve allows the concentration or composition of a material to be further determined.

Like Kubelka-Munk, log (1/R) can be used to obtain the apparent absorbance spectrum, which can be used to ascertain spectral features more clearly.

Near Infra-Red Spectroscopy

Theory

Infrared spectroscopy (IR spectroscopy) utilises the infrared region of the electromagnetic spectrum; light with a longer wavelength (lower frequency) than visible light. The infrared portion of the electromagnetic spectrum is divided into three regions: the near-, mid-, and far-infrared.

The near-IR, named for its proximity to the visible spectrum, is approximately 14000–4000 cm^{-1} (700-2500 nm). In some literature, the near infrared region is further defined as 700-1100 nm, and the region from 1100-2500 is termed the short-wave infrared region (SWIR). The mid infrared range

[2] Shimadzu Corporation, 'ABC's of the Diffuse Reflection Method', accessed 11 May 2017, http://www.shimadzu.com/an/ftir/support/ftirtalk/talk1/intro.html.

is approximately 4000–400 cm^{-1} (2500 - 25000 nm), and the far infrared is approximately 400–10 cm^{-1} (2.5 – 1000 μm) and lies adjacent to the microwave region of the spectrum.[3]

When infrared radiation interacts with a molecule, energy is absorbed. There are three ways that a molecule can absorb radiation. The first is when absorption of energy leads to an increase in rotational energy of the molecule, the second is when the vibrational energy is increased, and the third is when electrons are raised to a higher energy level. Energy may be absorbed in a combination of two or all of these ways. In each case, the energy is quantised – i.e., only specific discrete amounts of energy are absorbed. It is these absorption patterns that are detected and analysed in the field of IR spectroscopy.

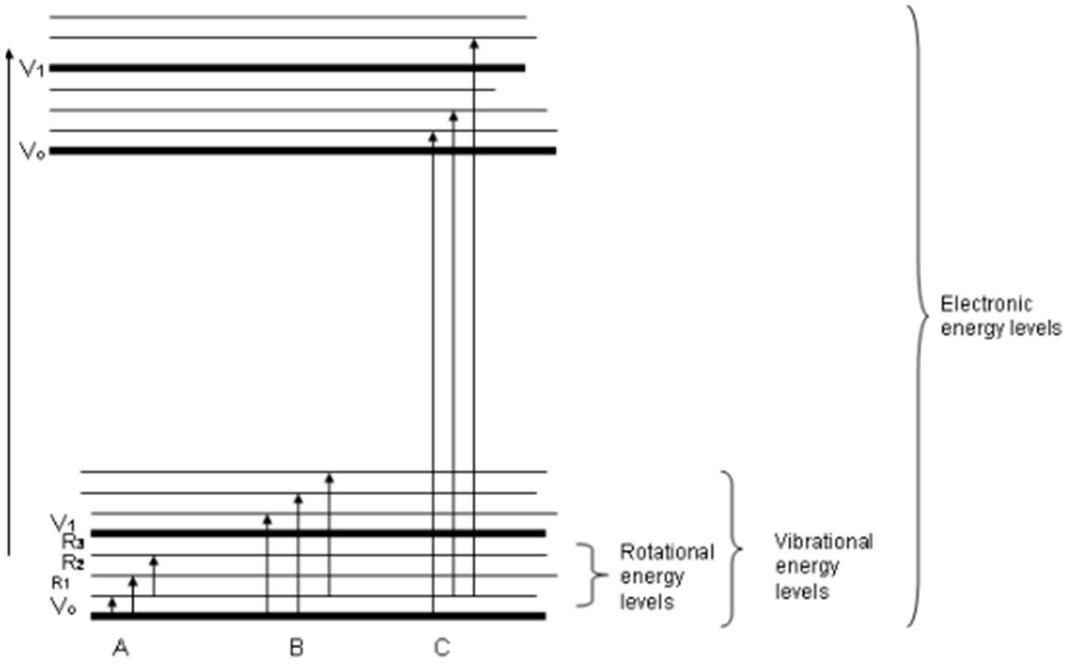

Figure 2: A diagram showing the order of magnitude of rotational, vibrational and electronic transitions.[4] (Please note that B is not technically correct as ΔJ is only + or -1).

[3] Warwick University, 'Analytical Equipment - IR, Near, Mid, Fourier Transform, N-IR, M-IR, FT-IR', accessed 16 February 2017, http://www2.warwick.ac.uk/services/ris/impactinnovation/impact/analyticalguide/ir/.

[4] Chemistry Libre Texts, 'Infrared: Theory', 2 October 2013, https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Vibrational_Spectroscopy/Infrared_Spectroscopy/Infrared%3A_Theory.

In the VIS and NIR parts of the spectrum (up to 1100 nm) absorption is due to electronic transitions. These can be transitions between delocalised molecular orbits, charge transfers, ligand field transitions among d-d orbitals and transitions from valence to conduction bands. These transitions require higher energy than those in the SWIR, where absorption is due to vibrational transitions, including combination bands and overtones.

A molecule can undergo many forms of vibration (symmetric, asymmetric and deformation are the most common). The more atoms (and therefore bonds) a molecule has, the more complicated the vibrational structure is. A molecule of 'n' atoms will have 3n-6 degrees of vibrational freedom (3n-5 if the molecule is linear).

When the energy of a frequency of radiation matches that of the vibrational energy of a molecule, it is absorbed by the molecule. The absorption induces a transition between two different energy levels. The absorbed radiation has a frequency that corresponds to the energy gap between the levels and can be expressed by Equation 3 where h is the Planck constant, v is the frequency, E_f is the energy in its final state after absorption and E_i is the initial energy.[5]

$$h\nu = E_f - E_i$$

Equation 3: The Bohr condition

However, molecules are only IR active (i.e. they only absorb radiation) if the vibrations cause a change in the dipole moment, in asymmetric stretching, for example. Symmetric stretching does not cause a dipole change in a homonuclear diatomic molecule, and thus is IR inactive. Similarly, in a homonuclear diatomic, there is no dipole moment, no vibrational transitions can occur, and the molecule is IR inactive.

The exact frequencies of light absorbed are determined by the mass of the component atoms and the strengths of the bonds involved, whilst the intensity of a peak depends on the change in the dipole moment and the number of specific bonds present. Individual bonds can cause individual peaks in the IR spectrum, but it is more common to see a peak representing a functional group. Overtones can occur; these are when a bond is excited to the second or higher energy state above the normal ground state. Combination bands in a spectrum can also be detected when more than

[5] E. Ciliberto and G. Spoto, eds., *Modern Analytical Methods in Art and Archaeology*, Chemical Analysis (New York: Wiley, 2000), p. 155.

one vibration is stimulated at the same time, and these are much weaker than the fundamental bands [6]

It can be common, due to the history of the field of IR, to show transmittance rather than absorption, in infrared spectra. However, for the purposes of studying pigments on manuscripts, diffuse reflectance techniques are used. Increasingly, wavelengths from the infrared, visible and ultraviolet parts of the spectrum are shone on the sample, and the full spectrum of the reference and sample are recorded and analysed by Fourier-Transform (FT) using a computer, rather than older dispersive methods. [7]

Published libraries

The most recently published and extensive library of visible reflectance is that published by Aceto et al. in 2014, and this is a source utilised often in this study.[8] Cosentino also published a similar data library paper in the same year, giving spectral information about pigments in different binders.[9] However, neither of these databases provide data for the infrared region above 1000 nm.

Cautions

As with many techniques discussed in this section, both VIS and SWIR FORS techniques and equipment have been adapted from industrial analysis to manuscript analysis. It is therefore imperative that any system, whether it is designed for a specific application, such as the Team Pigment equipment, or bought "off the shelf", is tested thoroughly to ensure that is can be safely used on manuscripts. In FORS analysis, it is vital that the power density of the visible and IR light is measured and kept to low limits of less than 0.5 $mWcm^{-2}$.[10] The system employed by Team pigment

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[6] Chemistry Libre Texts, 'Combination Bands, Overtones and Fermi Resonances', 2 October 2018, https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Spectroscopy/Vibrational_Spectroscopy/Vibrational_Modes/Combination_Bands%2C_Overtones_and_Fermi_Resonances.

[7] RSC.'Introduction to IR Spectroscopy - Learn Chemistry Wiki', accessed 16 February 2017, http://www.rsc.org/learn-chemistry/wiki/Introduction_to_IR_spectroscopy.

[8] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry'.

[9] Antonino Cosentino, 'FORS Spectral Database of Historical Pigments in Different Binders', *E-Conservation Journal*, 2014, 54–65.

[10] Andrew Beeby et al., 'There's More to Reflectance Spectroscopy than Lux', *Journal of the Institute of Conservation*, 8 May 2018, 1–12. Please note this paper includes L. Garner as co-author.

is regularly tested to ensure that the power density measured does not exceed this - the system regularly operates at around 0.45 $mWcm^{-2}$.

Laboratory experiments and equipment

The Team Pigment FORS equipment allows samples of pigment, or an area of a manuscript, to be illuminated by two 45° beams with a steady-output tungsten light source (Ocean Insight, formerly Ocean Optics HL-2000-HP). The wavelengths reflected are simultaneously collected by a 100 µm high-OH silica core optical fibre and collecting lens arranged to collect light scattered from the centre of the illuminated area with a diameter of 2 mm, placed orthogonally to the surface. In addition to the visible illumination - essential for visible FORS but also for accurate positioning - NIR wavelengths are also projected onto the area under analysis, delivered via a bifurcated fibre-optic with two high-OH 400 µm silica cores.

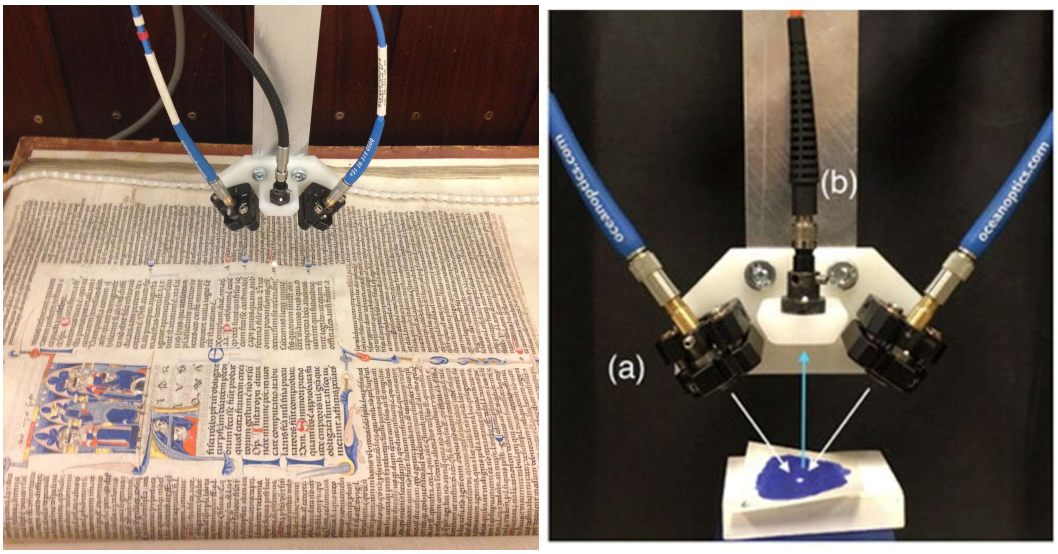

Figure 3: (left) Team Pigment's FORS head in action, and (right) a close up of the FORS head. The white spot ensures the collecting fibre-optic cable is positioned at the optimum height.

Although the FORS head now employed contains a microscope that allows photomicrographs of the area analysed to be taken, the prototype FORS head, shown in Figure 3, encapsulates the innovative nature of the design. Here, the overlapping spot of the two focussed 45° beams of light ensure the collecting fibre-optic cable is at the optimum height for collecting reflected wavelengths, whilst also limiting the accidental collection of specular reflection. Visible and NIR wavelengths are projected onto the page via a bifurcated fibre-optic cable (a) and are collected by a single fibre-optic cable

(b).[11] Most importantly, the FORS head is held steady by a gantry (not pictured) and has a working distance of approximately 5 cm away from the sample, meaning any area analysed does not need to be touched, and the FORS spectra can be collected non-invasively.

An OceanInsight (formerly OceanOptics) Maya2000Pro fibre-optic USB spectrometer processes the collected wavelengths. A schematic diagram of the inside of an OceanInsight Maya2000Pro fibre-optic USB spectrometer can be seen in Figure 4 below. Light enters the spectrometer via a fibre-optic cable that is plugged into the entrance aperture seen at A. The divergent beam of light is collimated by a concave mirror (B) and is then refracted by a (moveable) diffraction grating (X) onto another concave mirror (C) which focuses the spectrum on to a CCD (D). The CCD then digitises the spectrum received and relays it to the analysing software. In Team Pigment's case, this is a custom built LabView programme.

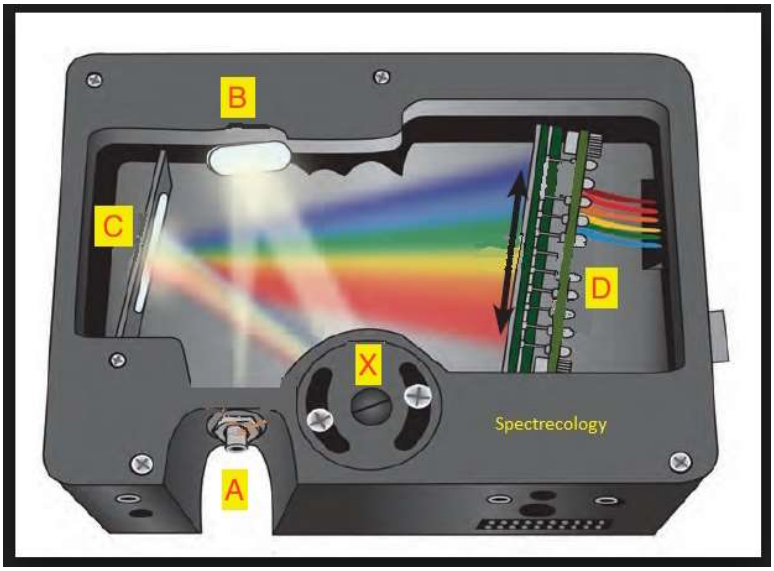

Figure 4: Adapted schematic diagram of the inside of a spectrometer.[12]

The reference spectrum from a clean Spectralon® tile was collected, as well as the dark spectrum, which was subtracted from the reflectance spectrum by the computer software. This allows

[11] More information about this design can be found here: Beeby et al., 145. Please note that L.Garner is a co-author on this paper.

[12] Spectrecology.com, 'Ocean Optics Spectrometers | Cuvettes | O2 Sensors', accessed 27 June 2020, https://www.spectrecology.com/.

correction to be made for background light, any dark current contribution, and the baseline. [13] Samples of pigments in raw powder form were prepared in the laboratory on a microscope slide, and their visible FORS spectrum recorded. R(λ) was determined by Equation 1.

The DRS spectrum of a sample of dark lapis lazuli solid powder from Cornelissen (product code: LC20001C) is shown below in Figure 5 and shows the sample reflecting more in the blue and NIR regions of the visible spectrum, whilst appearing pure blue to the naked eye. The DRS spectrum of a sample of dark smalt solid powder (Cornelissen LC20051C), which also appears dark blue to the eye, is shown below in Figure 6 and again reveals reflectance in the blue and red regions of the visible spectrum, but in a characteristically different way from the lapis lazuli spectrum.

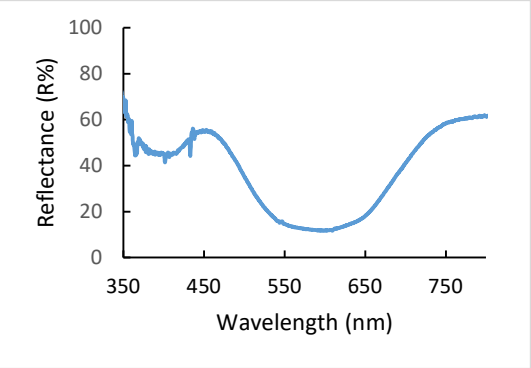

Figure 5: Diffuse Reflectance Spectrum of Lapis Lazuli

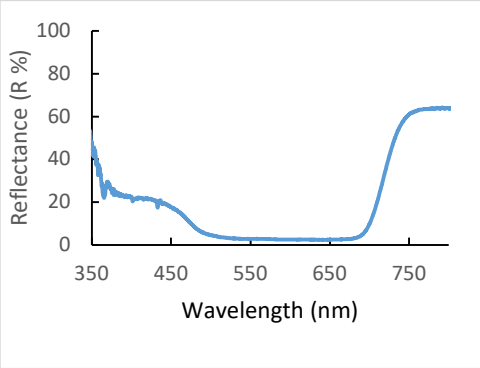

Figure 6: Diffuse Reflectance Spectrum of Smalt

In 2017/18 a new VIS-SWIR system was developed at Durham University by Prof. Andrew Beeby and was characterised by Hannah Hayler, an MChem student. Using LabView as an interface, the system measures and records the diffuse reflectance of a sample from 400 to 2500 nm, encompassing both the visible and the NIR range, marrying the data obtained in the visible region and processed by the Maya2000Pro, with data obtained from the infrared. The IR data is processed by ARCoptix FTIR OEM 100 module.

This system was employed to test the spectral resolution of a spot sample of pigment. A dot of azurite was painted onto 1 mm graph paper, fully covered by the VIS-SWIR system beam, and then progressively moving out of the beam 0.5 mm at a time. Azurite paint, in an egg white binder, was

[13] 'Subtracting Dark Spectra', *Ibsen Photonics* (blog), accessed 25 June 2020, https://ibsen.com/technology/detector-tutorial/subtracting-dark-spectra/.

chosen due to its characteristic NIR signal, as described above. The approximate area of the spot covered by the beam was assessed by eye, using the graph paper as a guide. The results of the experiment were recorded in Table 2, and the resulting spectra are shown in Figure 7.

Movement in the x-direction	Approximate area of dot illuminated
0 mm	100 %
0.5 mm	85 %
1 mm	60 %
1.5 mm	40 %
2 mm	10 %
2.5 mm	5 %
3 mm	2 %
3.5 mm	0 %

Table 1: Movement of dot and percentage of the area illuminated.

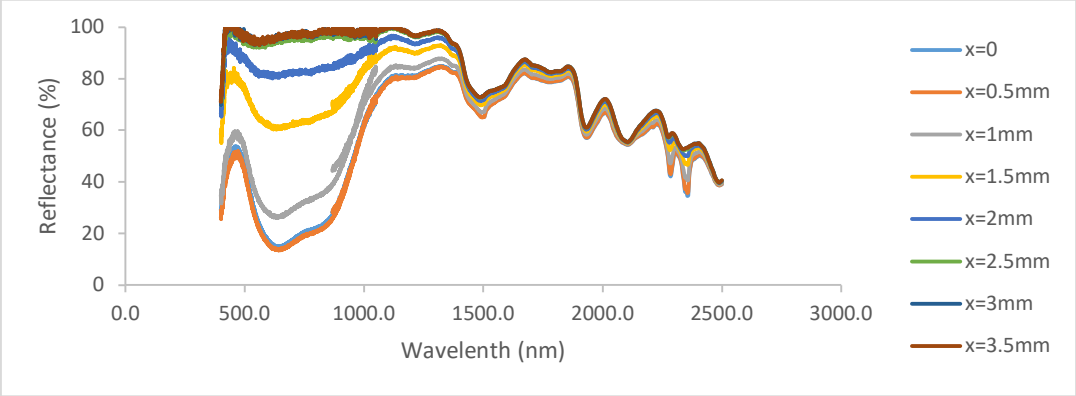

Figure 7: The reflectance spectrum of the azurite dot, as it moves progressively out of the beam. When x = 0 mm the spot is fully covered, and when x = 3 mm only 2 % of the spot of azurite is in the beam of light.

The portion of the spectra in the visible region tends towards a straight line with high reflectance as the proportion of white graph paper increases, as would be expected from the spectrum of white graph paper. In the infrared portion, the spectrum of azurite can be seen easily, until approximately 50% of the sample being illuminated with the beam. With less than 50% coverage, the spectrum is not clear and tends towards the spectra of blank graph paper. This is helpful as it gives an approximation of the area of a pigment that can be examined and result in a useful spectrum.

Kubelka-Munk Investigations

The dark blue pigment indigo was mixed with the white salt potassium chloride (KCl) in different concentrations, to produce five samples of slightly different shades of blue, as shown in Figure 8. The concentrations of the five samples are shown in Table 2.

Figure 8: Samples of indigo and KCL of differing concentration a (darkest) – e (lightest)

Concentration (% by weight)

A (Darkest)	3.5
B	1.6
C	1.1
D	0.6
E (Lightest)	0.2

Table 2: Concentration of samples A-E.

The diffuse reflectance spectrum of each sample was taken, and the spectra produced are shown in Figure 9.

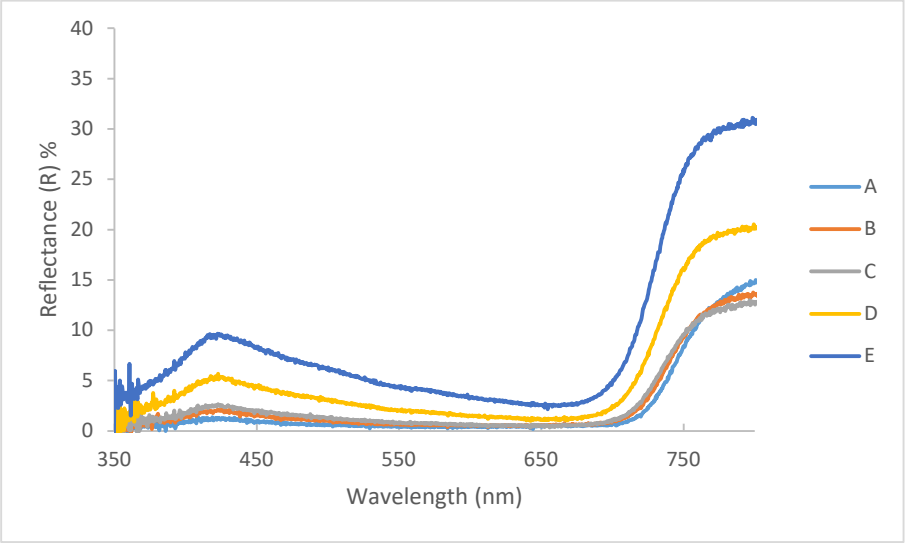

Figure 9: Diffuse reflectance spectra of 5 different concentrations of indigo in potassium chloride. A is the darkest solid and E is the lightest.

As can be seen in Figure 9, the lightest sample reflects the most light with the most reflectance in the red and blue wavelengths, as would be expected for a blue pigment. Conversely, the darkest sample reflects less light but still has signature indigo peaks in the red and blue areas of the spectrum. The absorbance maximum of indigo given in published literature is 660 nm and, as the concentration of indigo decreases (and so the pigment lightens), the maximum tends away from 660 nm.

The wavelength 424 nm was then chosen as a point in the spectra where all the reflectances are clearly separated, and there was little noise. The reflectance at this wavelength was recorded and the Kubelka-Munk equation applied to each concentration. The output was then converted into a percentage to match the data output by the DRS system (as described above). This is shown in Table 3.

Concentration by % weight	Reflectance (%)	KM value
3.5	1.2	4207
1.6	2.0	2396
1.1	2.4	1963
0.6	5.3	853
0.2	9.4	436

Table 3: KM values of the reflectance of 5 samples at 424 nm.

By plotting the reflectance percentage against concentration, as shown in Figure 10, a graph is produced showing a clear relationship between the two, although the relationship is not proportional.

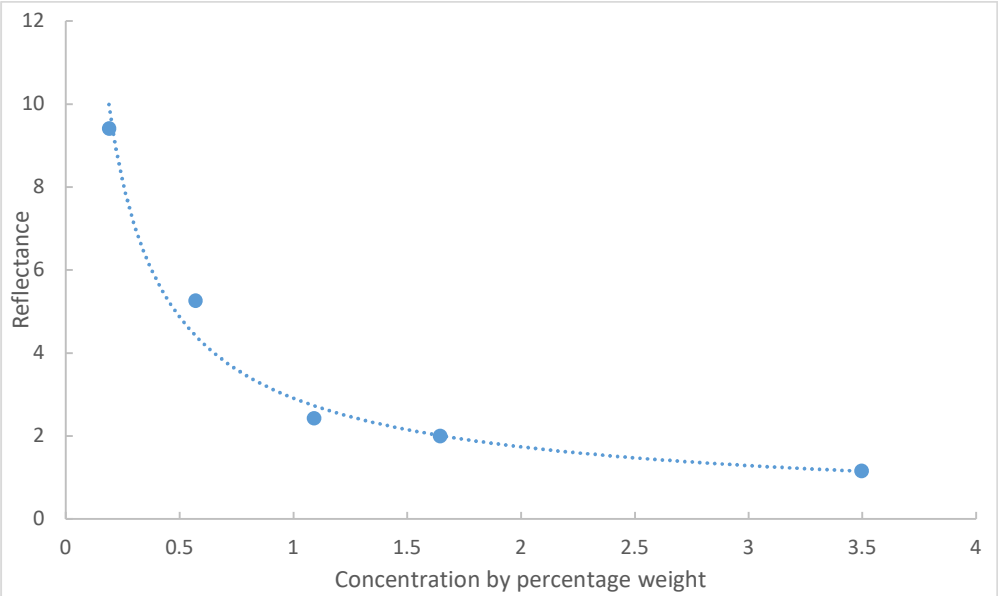

Figure 10: Concentration vs. reflectance of 5 samples of indigo at 424 nm

However, by utilising the Kubelka-Munk transformation, and plotting those values against concentration (Figure 11), the relationship can be seen to be approximately proportional to the absorption coefficient.

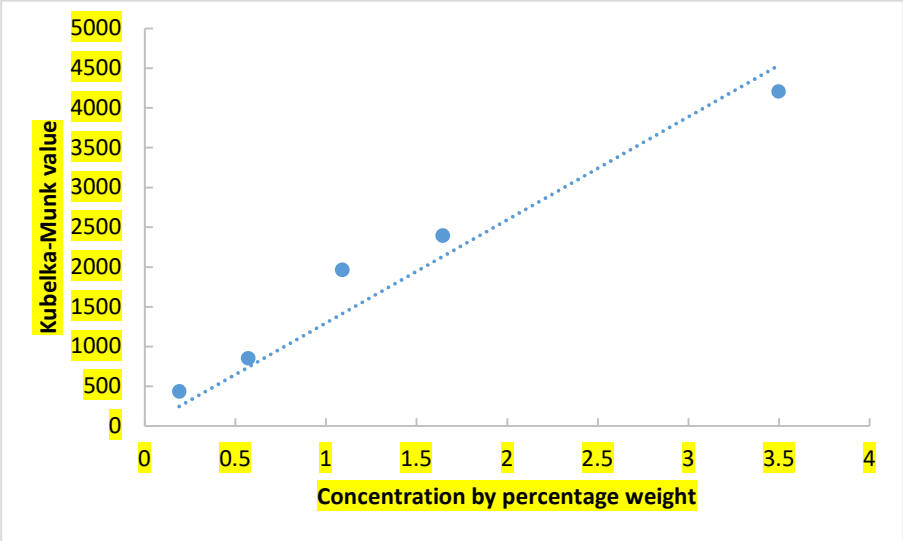

Figure 11: Kubelka-Munk value vs. Concentration of 5 samples of indigo in KCl at 426 nm.

Raman Spectroscopy

History

Chandrasekhara Raman was an Indian scientist who became intrigued with the phenomenon of light scattering in the sea. In 1930, using rudimentary equipment by today's standards, he won the Nobel Prize for his discovery that light scatters in liquids and gases both at the incident wavelength and with modified wavelengths. His work is sometimes described as an optical analogue to the then recently discovered Compton effect, which relates to the scattering of X-rays.

Explanation

Most light that interacts with matter undergoes Rayleigh scattering (elastic scattering) whereby a photon of light is absorbed by a molecule and is emitted again with no energy change. However, approximately 1 in 10^7 photons undergoes a form of inelastic Raman scattering, known as Stokes or anti-Stokes scattering. In Stokes scattering, a photon is absorbed and excites the molecule to a higher virtual energy state. The molecule then releases a photon of a different, lower frequency. In anti-Stokes scattering, the molecule loses energy and the photon emitted is of a higher frequency than the incident light. (See Figure 12.) The frequency of the photon emitted changes by the difference in energy between two vibrational/rotational energy states. By knowing the precise frequency of the incident light, and measuring the different frequency of the photons emitted after undergoing Stokes or anti-Stokes scattering, the Raman shift can be deduced.[14]

[14] P. W. Atkins and Julio De Paula, *Atkins' Physical Chemistry*, 9th ed (Oxford; New York: Oxford University Press, 2010), p. 431.

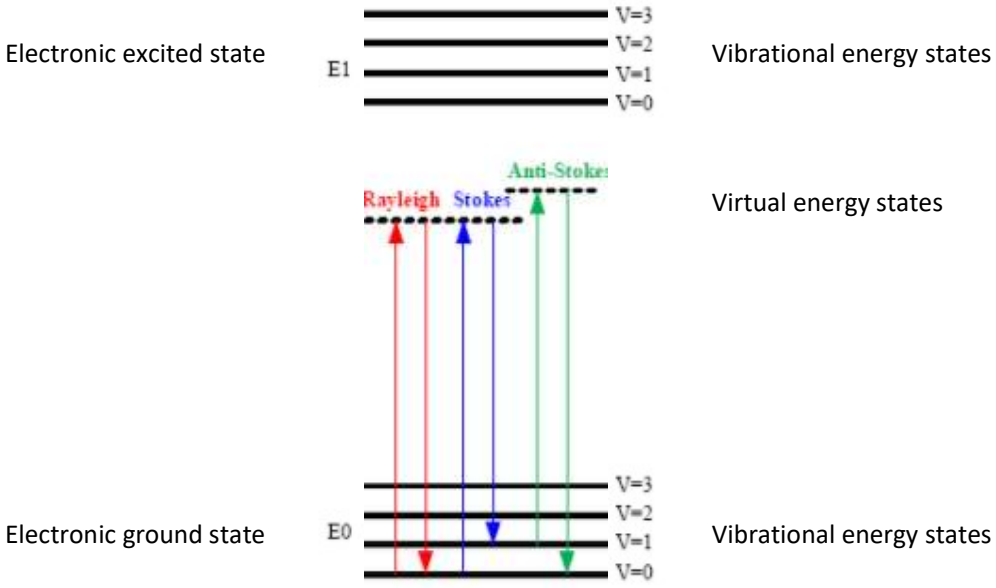

Figure 12: Rayleigh and Raman (Stokes and anti-Stokes) scattering.

In Figure 12, the energy level diagram of the scattering processes is shown. For a normal Raman scattering process, a molecule is excited from its ground state (E0) to a virtual state when illuminated by incident radiation, such as a laser. Since a virtual state is not a specific quantised energy level, it will decay very fast with the emission of a photon. For Stokes Raman scattering, the initial state of a molecule is the lowest vibrational state of the ground state (E0, v = 0). Anti-Stokes Raman scattering starts from the higher vibrational energy level (E0, v = 1) of the ground state and returns to a lower level (E0, v=0).

Using Raman Spectroscopy in Sample Analysis

In order to identify molecules that make up the pigments in a medieval manuscript, a low-powered laser is used to provide photons of an exact frequency. Most importantly the laser must be sufficiently low-powered (i.e. in the order of 0.1 - 0.5 $mWcm^{-2}$) that the manuscript surface is not heated by more than 1°C, in order to avoid degradation of the manuscript. In addition, the incident frequency must be the optimum to excite the molecules in the sample; the frequency of the laser can be changed in order to identify different molecules that respond differently with different wavelengths. Each molecule has a different set of vibrational energy levels, and so Raman Spectroscopy uses Stokes scattering to deduce the vibrational and rotational modes of the sample in question and produces a spectrum with peaks, attributed to different molecular vibrations and/or rotations. When these are identified and compared to library data, this provides information on the molecular make-up, and hence identification, of the pigment.

Molecules occupying a given vibrational mode at a given temperature follow a Boltzmann distribution, so at room temperature, which is the optimum storage temperature for manuscripts, Stokes scattering is more frequent than anti-Stokes scattering as more molecules are at their "ground state". Therefore, it is more usual to measure this value as opposed to the anti-Stokes value as a larger signal can be obtained.[15]

Infrared spectroscopy can produce similar results and can be more sensitive than the Raman effect; although it cannot identify vibrations in symmetrical molecules and so in these cases Raman Spectroscopy can yield more meaningful information.

Raman spectroscopy, therefore, provides a 'fingerprint' for many commonly encountered compounds and has been described as 'the most specific, spatially refined and immune to interference' method for analysis of samples of this type.[16] There have been recent advancements in the use of micro-Raman where the technique is deployed in conjunction with an attached microscope, providing information on the smallest areas of an illumination. Laser beams as small as 5 μm in diameter can be focussed on to the surface under examination, in some cases identifying areas as small as a single crystal. Furthermore, the development of portable Raman systems means that the technique is becoming increasingly utilised, allowing more manuscripts to be analysed and libraries of data to be increasingly refined.

[15] Zhiyun Li et al., 'Raman Spectroscopy for In-Line Water Quality Monitoring—Instrumentation and Potential', *Sensors* 14, no. 9 (16 September 2014): 17275–303, p. 276.

[16] Robin J. H. Clark and Peter J. Gibbs, 'Raman Microscopy of A 13th-Century Illuminated Text', *Analytical Chemistry* 70, no. 3 (February 1998): 99A-104A, p. 276.

Raman spectrometer set-up

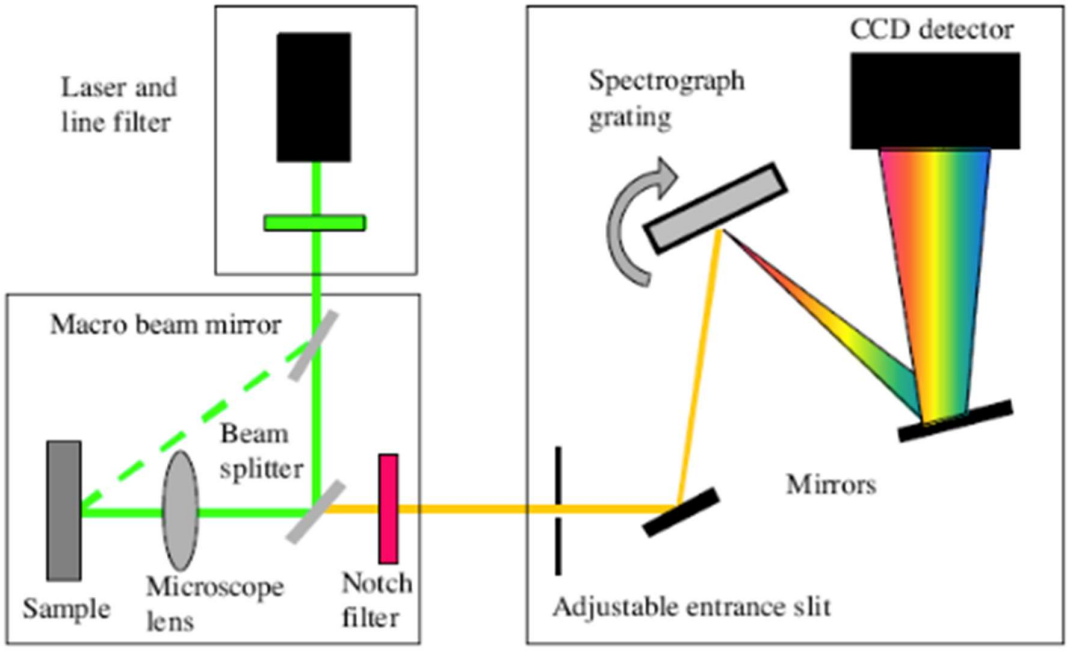

Figure 13: A diagram of a Raman Spectrometer.[17]

Figure 13 shows a schematic example of a Raman instrument. In this system (as in Team Pigment's portable system) the laser is focused onto the sample with a microscope objective and the Raman scattering is collected through the same. The Raman signal is passed through a collection lens and then a notch filter to remove the Raleigh and Anti-Stokes scattering. The required Raman scattering passes through a slit and reflects off a holographic grating. This refracted light is then projected onto a CCD (a charged coupling device). Photons that land on the CCD induce a charge that can be interpreted by software into a Raman spectrum. [18]

[17] University of Pennsylvania, 'The Raman Spectrophotometer', accessed 15 May 2020, https://www.sas.upenn.edu/~crulli/TheRamanSpectrophotometer.html.

[18] Andor Learning Centre, 'Instrumentation for Conventional Raman Microscopy and Total Internal Reflection Raman Microscopy', accessed 15 May 2020, https://andor.oxinst.com/learning/view/article/instrumentation-for-conventional-raman-microscopy-and-total-internal-reflection-raman-microscopy; University of Pennsylvania, 'The Raman Spectrophotometer'.

Limitations

Raman Spectroscopy is particularly useful in the identification of inorganic compounds and produces good results even when the substance under investigation is present in very low quantities. However, Raman can be challenging to use with organic compounds, such as madder or red lac, as these substances fluoresce, dwarfing the Raman signal and masking any distinguishing features.

Raman spectroscopy can be conducted with a range of excitation wavelengths. However, compounds respond differently to the exciting wavelength chosen due to resonance effects as well as their colour and whether or not they are organic, for example, so choosing a sub-optimal wavelength laser source means definitive identification can be tricky. Comparison data is required, and it must be ensured that the library data utilised was collected with the same wavelength as the sample.

Published libraries

One of the most commonly used Raman spectra libraries is that compiled by Robin Clark et al. in 1997. This details the spectra of 56 pigments collected with both a red HeNe laser and green argon-ion laser used with wavelengths at 632.8 and 514.5 nm respectively. Spectra are arranged into a library where pigments can be located by colour and by strong bands observed.[19] An additional paper was published in 2001, which extended this database by 22 spectra and included varnishes and binders and used four different laser excitation wavelengths.[20]

A more recent paper published by Northumbria University by G. Marucci et al., as part of Team Pigment, recreates and improves upon the previous data by suggesting which excitation wavelength (1064, 780.0, 647.1, 632.8, or 514.5 nm) is the best choice to achieve the clearest spectrum for each pigment, and provides spectra for 31 pigments at each of these wavelengths.[21] It is this library data that is used extensively for the research on seven thirteenth-century bibles in Chapter Four.

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[19] I. M. Bell, R. J. Clark, and P. J. Gibbs, 'Raman Spectroscopic Library of Natural and Synthetic Pigments (Pre-Approximately 1850 AD)', *Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy* 53A, no. 12 (15 October 1997): 2159–79.

[20] Lucia Burgio and Robin J.H Clark, 'Library of FT-Raman Spectra of Pigments, Minerals, Pigment Media and Varnishes, and Supplement to Existing Library of Raman Spectra of Pigments with Visible Excitation', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 57, no. 7 (June 2001): 1491–1521.

[21] G. Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', *Analytical Methods* 10, no. 10 (2018).

Calibration and error

When any Raman system is set-up, it is usual to calibrate the system with an atomic resonance lamp. In this work, a low-voltage powered neon lamp was used since this produces a spectrum with peaks across a range of wavelengths spanning the region of the Raman spectrum obtained when using 633 nm excitation. To adjust the system, the spectrum of neon is recorded, and the Raman software is given the exact Raman shift of where the neon peaks should be so that the software can adjust the calibration of the instrument to ensure peaks are recorded at the correct wavenumber. Calibration is particularly crucial on a portable system that is moved, set up, and set down several times a week.

Although the Raman system does not have any moving parts, (aside from the spectrograph grating which moves during calibration), errors can be introduced to the position of peaks in the spectrum by temperature changes in the equipment, temperature changes in the laser, and temperature changes in the specimen. Expansion of optical components can introduce errors of several wavenumbers.[22]

In a portable system that is used heavily and under time pressure, experimental errors are inevitable. In addition, when considering background removal (see below), this error is likely to be increased. Therefore, this study has chosen to use 10 cm^{-1} as an acceptable deviation from published data.

Background removal

Every Raman spectroscopy system, like any analytical equipment, is affected by undesirable 'noise' and a varying background (or baseline) that interferes with instrument calibration and the spectral information it produces. In the analysis of pigments, the fluorescence of organic dyes, binders and the parchment also contributes towards obscuring any potential peaks. When not saturated or swamped with fluorescence, the noise and background are usually of a lower frequency that the analyte signal, but as they are always changing it can often be difficult to differentiate between noise and signal, and can be difficult to remove the background to leave only the signal.[23]

Several papers have been published that examine solutions to this problem; the method applied in

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[22] Didier Hutsebaut, Peter Vandenabeele, and Luc Moens, 'Evaluation of an Accurate Calibration and Spectral Standardization Procedure for Raman Spectroscopy', *Analyst* 130, no. 8 (14 July 2005): 1204–14.

[23] Seong-Joon Baek et al., 'A Simple Background Elimination Method for Raman Spectra', *Chemometrics and Intelligent Laboratory Systems* 98, no. 1 (15 August 2009): 24–30.

this study uses a non-quadratic function to minimise and remove the background. In the MatLab script "Backcor" the user estimates the background with a lower-order polynomial of their choosing and, once best fit is observed, the background is removed.[24] An example of background and fluorescence removal can be seen in Figure 14 below, where the two carbon peaks at 1348 and 1590 cm^{-1} are not distinguishable in the raw spectrum, but can be identified in the processed spectrum.

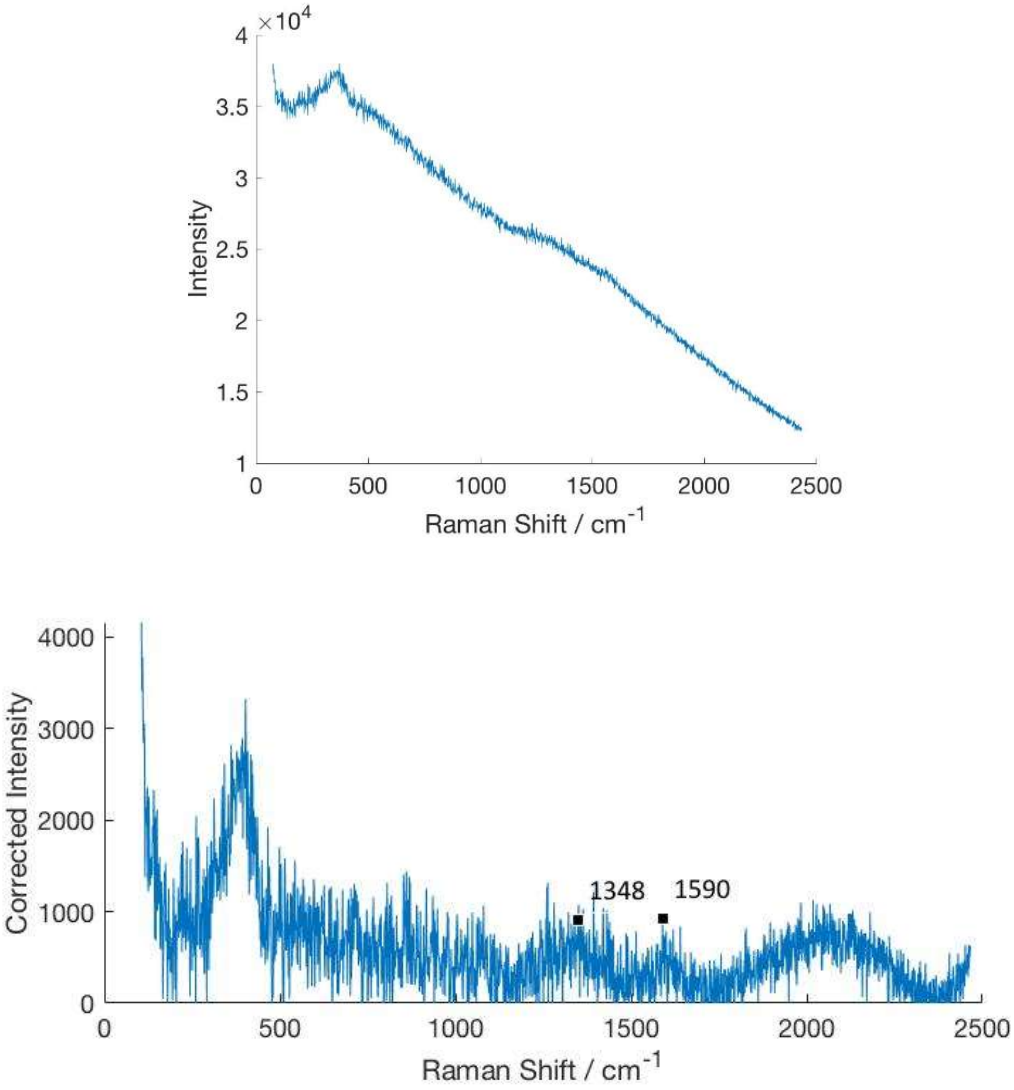

Figure 14: (top) The raw Raman spectrum of carbon, and (bottom) the processed spectrum.

[24] Vincent Mazet et al., 'Background Removal from Spectra by Designing and Minimising a Non-Quadratic Cost Function', *Chemometrics and Intelligent Laboratory Systems* 76, no. 2 (April 2005): 121–33.

No background removal tool is perfect, and it has been noticed during this study that the use of "Backcor" sometimes introduced artefacts into the spectrum that were not present in the raw spectrum, especially when there is a lot of fluorescence, and also that occasionally peaks visible in the raw spectrum were translated by a few wavenumbers in the processed spectrum. An example of this phenomenon can be seen in Figure 15 where an artefact centering on approx. 1300 cm^{-1} is introduced. Furthermore, occasionally some peaks, visible in the raw spectrum, do not appear in the processed spectrum. Where this occurs, a comment is made in the describing text.

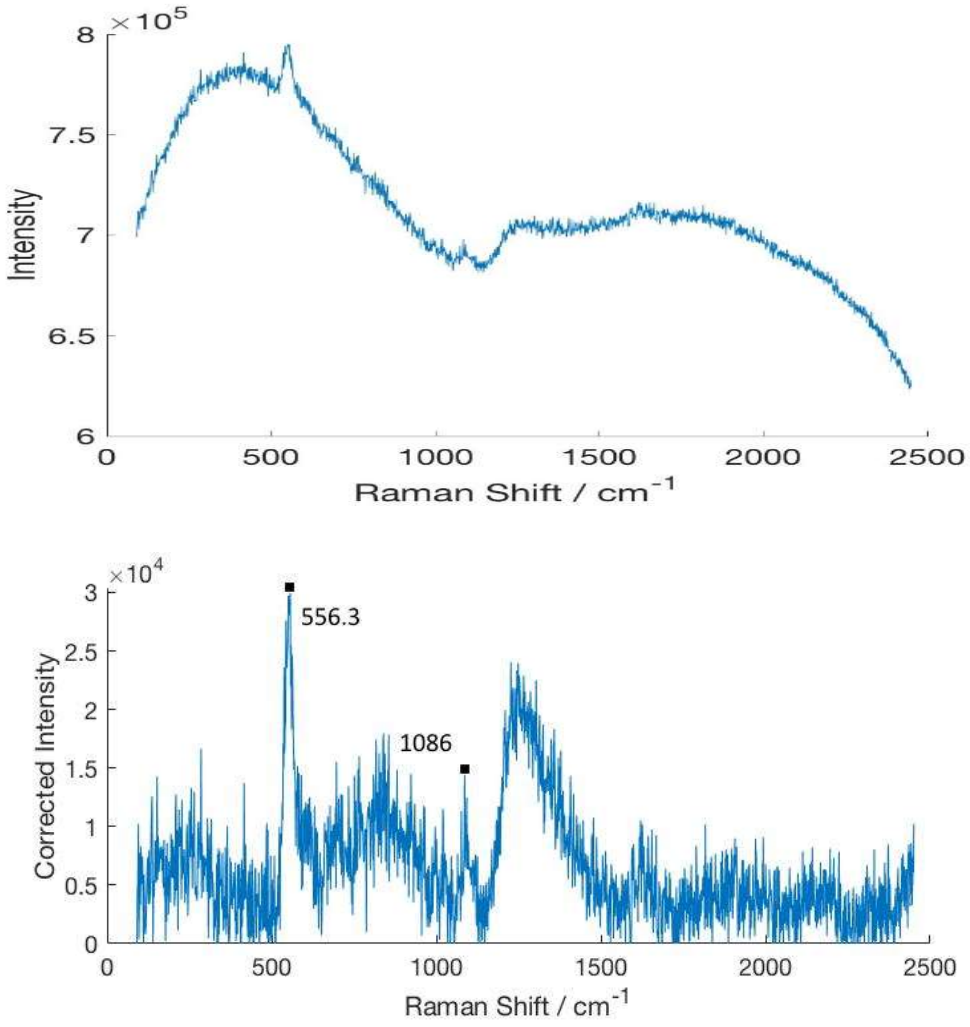

Figure 15: (top) A raw Raman spectrum of lapis lazuli, and (bottom) the processed spectrum.

Laboratory Experiment and Equipment

The work described in this study utilises two Raman spectrometers. One is a static laboratory spectrometer situated in the laboratory at the Chemistry Department at the University of Durham, and the other is portable. The portable equipment is the equipment used to collect the data examined in Chapter Four.

Static system

The static laboratory system is a Horiba LabRam HR, equipped with a red 632.8 nm He-Ne laser and a 532.0 nm frequency-doubled Nd:YAG laser. This system is equipped with a 'free space' microscope providing control and focus in the z-axis whilst a joystick-controlled translation stage provides fine control in the x-y. The maximum power at the sample is <0.35 mW. A Peltier-cooled CCD array provides a signal to the Horiba Labspec 6.0 software that controls the instrument.

Portable

The portable system employs a red diode laser operating at 632.8 nm and 1 mW, which is delivered through a fibre-optic to a Horiba Superhead or home-made Raman probe which delivers the laser to the page via a Nikon ELWD 40x microscope lens which also collects the backscattered Raman signal. The lens enables the head to sit approximately 10 mm above the page. A photograph of the set-up can be seen in Figure 16.

The power of the laser is tested before each run of samples is taken and is usually found to be < 0.3 mW, with the laser spot estimated to be about 50 µm in diameter. A previous laboratory test using an infrared camera estimated the temperature rise on the page due to the laser to be < 1°C at <0.3 mW. The collected scattered light was transferred down a second fibre-optic cable to an Andor Shamrock 163 spectrograph equipped with a 1200 g/mm grating and an Andor Newton 920 EM-CCD camera operating in 'normal readout' mode, that was controlled by Andor software. The system was checked for calibration using a neon lamp and compared to its standard spectrum. The Raman sampling head is attached to a gantry to allow movement over the page of the book and also contains a Veho Microscope and camera to allow a photograph of the precise spot of the laser sampling area to be recorded.

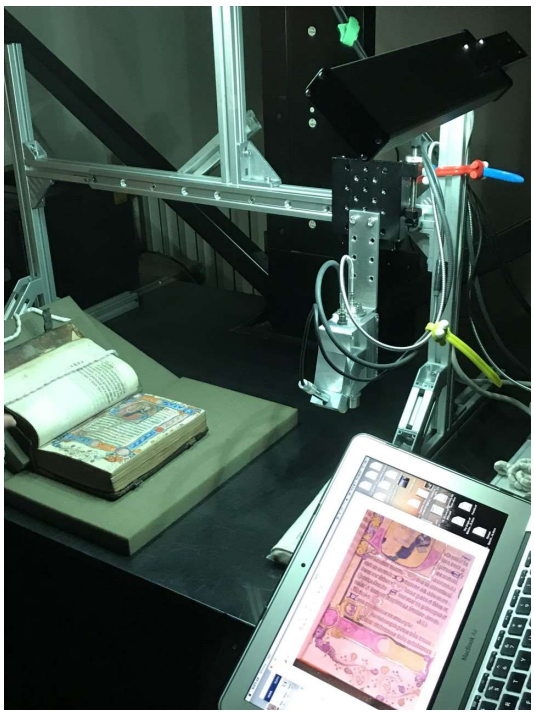

Figure 16: A photograph of the gantry over the manuscript. The Raman super-head is attached to the slider.

Imaging Techniques

Spectral imaging

Spectral imaging was first developed as a remote sensing method utilised in astrophysics and for military purposes. The positive applications of the method as a non-invasive and relatively quick method of data collection were soon recognised and put to use in environmental fields, medicine, food science and quality control, and agriculture. Increasingly, the methods are applied to conservation and heritage science.[25]

Spectral imaging is a fusion of both imaging and spectroscopy. A surface imaged in 2D produces a matrix I x J, where I is the number of pixels along the x-axis and J is the number of pixels along the y-axis. If I x J = K, then K number of pixels exist. An image is a record of the light intensity of K number of pixels. Spectroscopy measures the intensity of light as a function of wavelength, at a single point. If a detector has K pixels, then K intensity values will be recorded at a given wavelength.

The definition of multispectral and multispectral imaging can be difficult to pinpoint, as much depends on the field of use and application. In multispectral imaging K number of light intensities are recorded, one for each pixel. This is repeated for the image under different discrete wavelengths of light. In hyperspectral imaging, the wavelengths that the image is subjected to are not discrete and can be so numerous that they can be thought of as a continuous spectrum. K number of pixels record the light intensity data across the spectrum, and therefore any pixel individually produces a reflectance spectrum. The data produced can be thought of as a cube (see Figure 17).

[25] Haida Liang, 'Advances in Multispectral and Hyperspectral Imaging for Archaeology and Art Conservation', *Applied Physics A* 106, no. 2 (February 2012): 309–23.

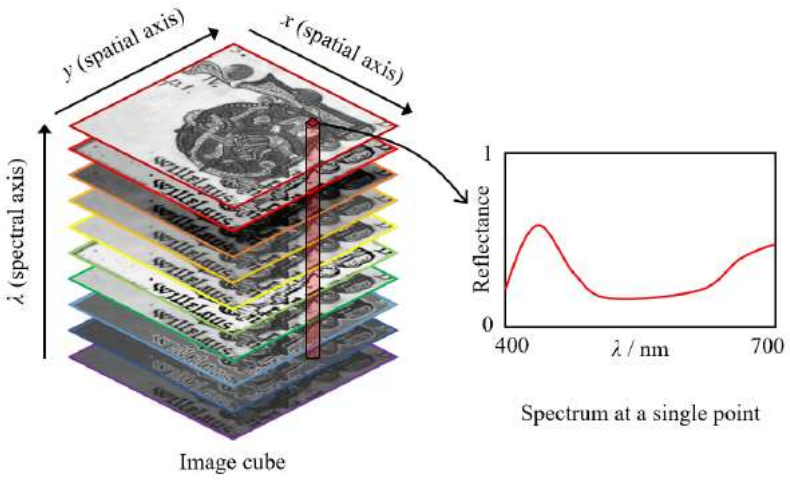

Figure 17: A representation of an image cube, and an extracted reflectance spectrum at a single spatial position[26]

There are different methods of collecting spectral imaging data: point-scanning, line-scanning, area scanning and single-shot. The method that Team Pigment use is multispectral area scanning – a surface is imaged in 2D at nine discrete wavelengths.

The advantages of area scanning are that it is a quick way of recording nine 'spectra' from each pixel of an image. It takes roughly 10 minutes to acquire nine images (and therefore nine spectra per pixel) of an area 20 cm x 20 cm approx. In addition, no movement of either detector or surface required, as is required with point-scanning and line-scanning.

Team Pigment Multispectral imaging set up

The Team Pigment system uses a Canon EOS-60D 24-megapixel camera, modified for operation in UV-NIR wavelengths. The system is used with a Jenaoptic apochromatic lens set high enough above the manuscript to capture a full page of a medium-sized manuscript. The apochromatic lens focuses different wavelengths of light at the same focal length, which is imperative when nine different wavelengths of light from 400 - 850 nm are used to photograph the same page.

The different wavelengths under which an image is captured (λ = 400, 450, 500, 550, 600, 650, 700, 750 and >850 nm) are achieved by the use of 25 nm bandpass filters (apart from the last filter which

[26] Image reproduced with kind permission from Alice Merryweather's MChem dissertation 'Development of a VIS-NIR Hyperspectral Imaging System for the analysis of Medieval manuscripts', Durham Chemistry 2018.

uses a long-pass filter) used in combination with LED illumination. The filters are set into an Atik EFW-2 filter wheel controlled by a LabView program.

Whilst some cameras and lenses might be better performing in different situations and set-ups, this system is designed with ease of portability, function, and cost in mind. A picture of the set-up can be seen in Figure 18 below. As can be seen, two strip LED illuminators - that can produce light of variable wavelengths - illuminate the manuscript page, whilst the camera and lens sit atop the filter wheel above.

Canon's EOS Utility software allows the camera to be activated remotely, which is vital as it prevents camera shake and movement during long-exposures. Most images taken are saved in a RAW and JPG format. A custom-made LabView program controls the filter wheel, again from a distance.

Figure 18: The Team Pigment multispectral imaging set-up.

Applications

Spectral images

Once obtained, multispectral images can reveal much interesting information, some of which can be gleaned simply from looking at the raw images taken under different wavelengths. As can be seen in Figure 19 below, comparing the infrared image of NCO MS. 20 *fol.* 1*r* with the colour image allows

the properties of certain pigments under near infrared light to be seen, aiding pigment identification, and allowing further information about the artistry to be discovered. In this case, the blue lapis lazuli that colours the initial is pale in the IR whereas the blue azurite that colours the paraphs is dark.[27] The carbon lines which outline the figure at the bottom and the descender of the initial can more easily be seen as they are dark in the IR, whereas these are not able to be distinguished in the colour image. Interestingly the correction seen in the margin at the top right of the colour image is practically invisible in the NIR, whereas the rest of the text can be seen. This suggests that the correction was added in different ink, and thus was either added at a different time, or by a different hand.

Near infrared images examined prior to further analysis of pigments make an excellent 'triage' system to get an overall idea of some of the pigments present and where, and which areas require which type of further investigation. The image in Figure 19, for example, gives a clear indication that carbon is used to outline the artwork, as it is dark in the near-infrared, and also that azurite is used for the paraphs in the text, as they too are dark in the near infrared image. This image is examined more closely in Chapter 4.

Figure 19: NCO MS. 20 fol. 1r (left) colour image taken in daylight (right) infrared image.

Multispectral images can be manipulated to recreate a colour image. If the images taken under 450, 550 and 650 wavelengths are thought of as channels of red, green and blue (RGB) then merging the

[27] See Appendix 5G for further details on the analysis of these colours.

RGB channels will reproduce a reasonable representation of the original colour image, as illustrated by Figure 20.

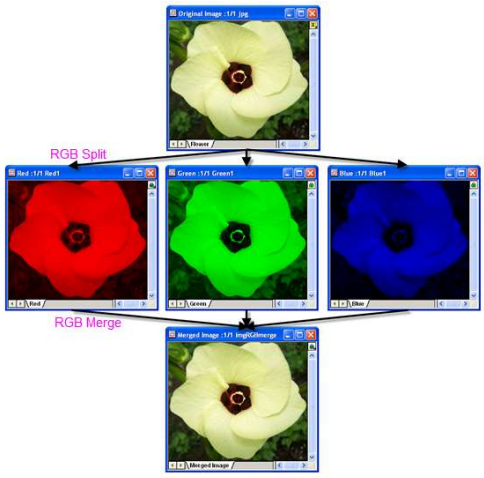

Figure 20: An image split into RGB channels and then recombined.[28]

False-colour NIR images

Furthermore, another way that these colour images might be manipulated is to use them as a reference image for comparison against a false colour image. In order to produce a false colour image, rather than combining the RGB channels to create a colour image, the red channel is swapped for a near infrared image, and the green channel is swapped for the combined red and green image data with the blue channel remaining as the blue data. [29]

Figure 21 below shows fol. 15r, The Annunciation, from Lambeth Palace MS 474 (The Hours of Richard III). In the left image, a standard colour photograph of the manuscript is displayed, showing the Blessed Virgin Mary within a decorated initial, and an ornate decorative border. Mary's robes are azurite, a blue pigment in visible light, which strongly absorbs near infrared wavelengths. The border contains lapis lazuli, a blue pigment in visible light but that reflects near infrared wavelengths. In the right-hand image, the differing use of lapis lazuli and azurite can easily be seen. As lapis lazuli reflects blue and NIR wavelengths but absorbs red and green, it

[28] originalab.com, 'ChannelSplit_Merge.Png (547×537)', accessed 15 May 2020, https://www.originlab.com/www/products/images/ChannelSplit_Merge.png.

[29] See Appendix A for the MatLab code for this process.

appears pink - thus the blue decoration in the border of the ordinary photograph becomes pink. In contrast, azurite absorbs green, red and NIR wavelengths and therefore appears blue - hence Mary's robes are blue.

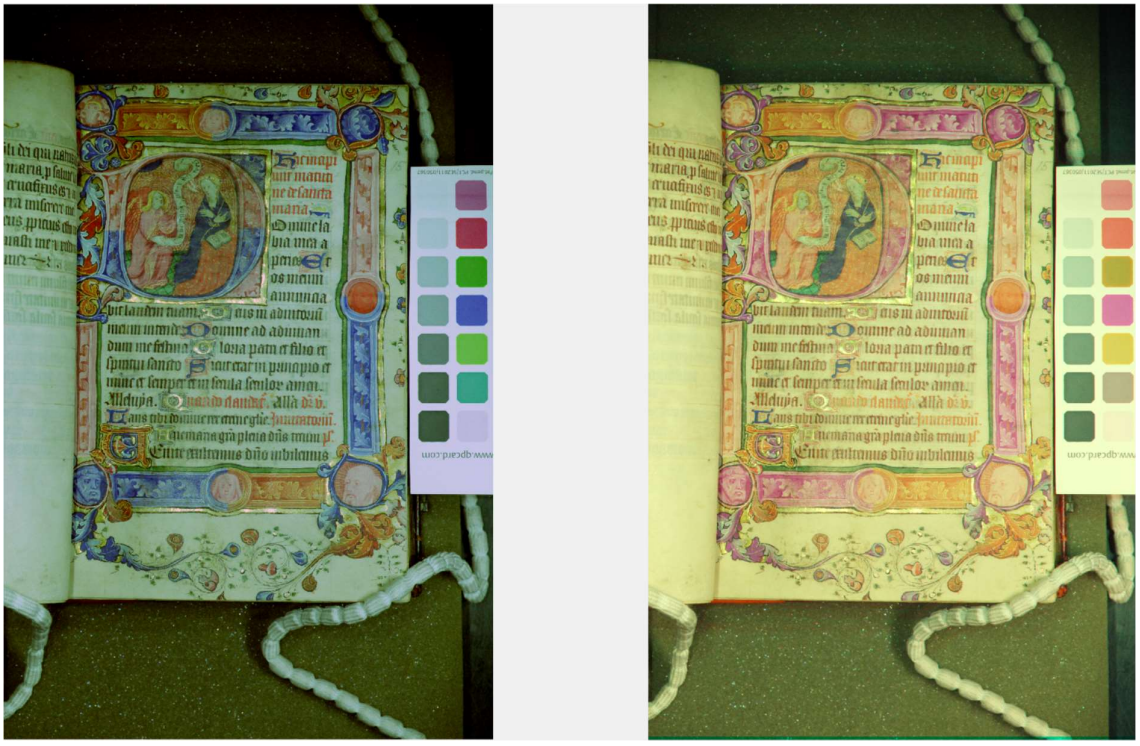

Figure 21: (left) A colour photograph of fol. 15r and, (right) a false colour image.

Microscopy

Microscopy, the use of a microscope to view a magnified image of part of a manuscript, is a widespread tool that is used often by conservation professionals and manuscript researchers, as microscopes are easy to use and yield much interesting information from images viewed.

Figure 22: Team Pigment's stereo-microscope in use.

Team Pigment Microscope Equipment

Team Pigment have a stereo-microscope, shown in action in Figure 22, which is a microscope that has two eyepieces and an objective lens slightly offset from one another, rather than a single objective employed by conventional microscopes. This arrangement provides a stereoscopic view of the object and allows the user to see and understand more of the 3D nature and textures of the object viewed. Illumination is provided by a circular lamp assembly attached to the microscope and offers the viewer four choices of wavelength under which to image the manuscript – 365 nm (UV), a white LED (visible) and two infrared wavelengths – 730 nm and 980 nm. The Durham stereo-microscope is a VISISCOPE SZT350. The microscope has a Sony RX0, modified for UV-NIR imaging, attached, which is a compact, high-quality imaging camera with a 24 mm lens and a 15.3 megapixel output. Measuring just 59 x 40 x 30 mm it is an ideal size to attach to a microscope viewer to capture the detailed images seen although it does not capture a stereo image; an example of the magnification aspect can be seen in Figure 23.

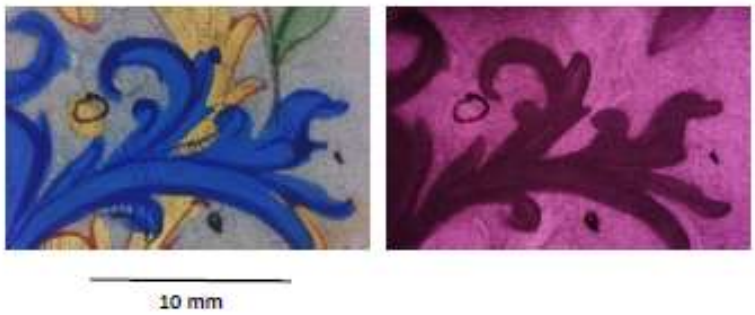

Figure 23: An example of a manuscript leaf image taken under white and infrared illumination, showing the size of the magnified image.

Applications of microscopy

Side Illumination

When used in conjunction with side illumination, as seen in Figure 24, the texture of the pigments on the page can very clearly be seen, meaning that the order of application and the intended effects of the painter can more easily be ascertained.

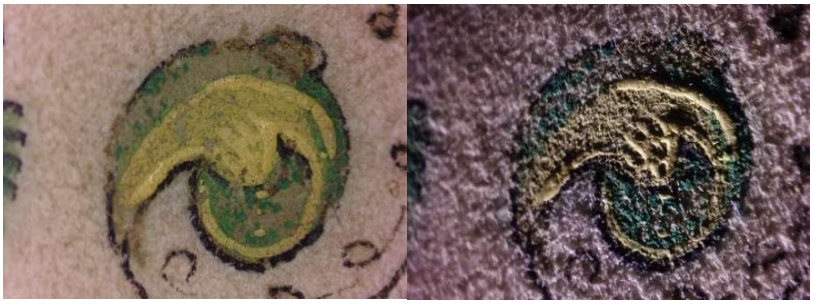

Figure 24: A foliate curl from GUL Hunter MS 252 (left) under the usual illumination and (right) under oblique illumination. The curl is approximately 5 mm in diameter.

In Figure 25, an area of parchment that has been degraded by a green copper-based pigment is seen. With side illumination, the 3D nature of the degradation as the copper 'eats' into the parchment fibres is seen easily.

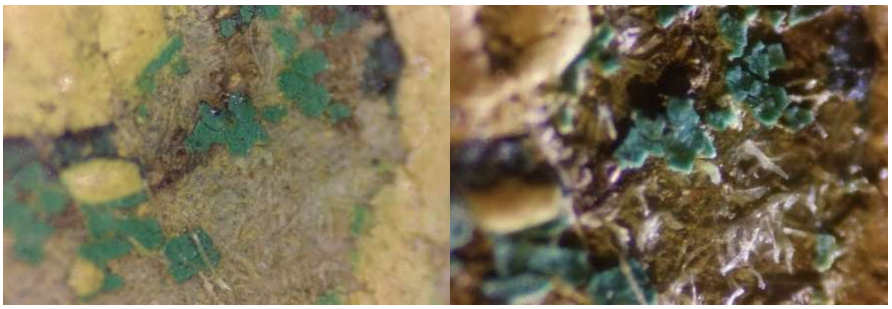

Figure 25: An image of copper degradation on parchment (left) under the usual illumination and (right) under side illumination.

This side illumination technique can be formalised and used to create virtual 3D images – see the section on RTI below.

Under-drawing

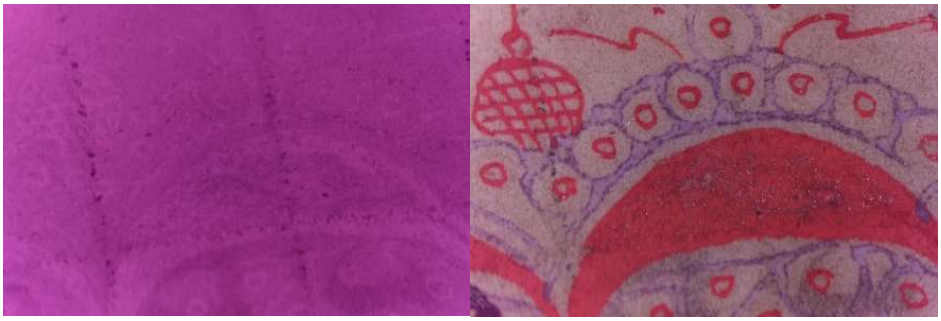

Figure 26: (left) Infrared image of lines drawn on the page - that are barely visible in the (right) visible image.

Infrared illumination, coupled with a microscope, can yield fascinating information about under-drawings and other marks made prior to the application of paint onto the parchment. In Figure 26, the lines scored on the parchment to provide the text guide can more clearly be seen, providing further information about the construction of the book.

Figure 27 shows *pentimenti* – in the IR image the artist's original drawing of where the hood, eyebrows, and ear were placed can easily be seen before the painter painted over the drawings to create his final version.

Figure 27: In DCL A.II.3 the visible image (left) covers the original drawing that can be more clearly seen in the (right) IR image. The original outline of the top of the hood is revealed.

Reflectance Transform Imaging

Theory

RTI exploits the fact that from a fixed viewing position light reflected from a surface depends on the direction of illumination. Several images are taken from the same fixed view, but with different angles of illumination, are combined in software that determines the surface normal of an object and produces a 3D image of a surface showing its topography. This image can be manipulated on the screen to provide a view of the object from any angle. The software can be further manipulated to provide contrast, specular enhancement, or both, producing 2D images that are greatly enhanced - as seen in Figure 28 below.

Figure 28: (left) An image of Gustavus Adolphus' seal (King of Sweden 1611-1632), (middle) the seal under a raked light with contrast, and (right) the seal with RTI specular enhancement.[30]

Limitations

Although images can be acquired rapidly once the equipment and target object are in place, arranging the set-up of the RTI recording system can be time-consuming. Provision needs to be made to illuminate the object from a 180° hemisphere above it, and angles of illumination must be recorded accurately. In addition, once set up the system needs to be able to be activated remotely - any shadow of a person operating the system will interfere with the images, plus any movement of the object, the camera or the lighting will also be detrimental.

Applications

This technique allows for close examination of the texture of the parchment and paints applied (similar to that in the microscopy section above) which can reveal information about the order of paint application, and the techniques of the artists. In addition, specular reflection from shiny gilded areas can be removed, whilst the surface changes that are produced when erasures are made can be seen more easily. Fine details such as paint or ink losses, or pooling can be seen. The 3D image created can be viewed on a screen or use to create a more detailed 2D image.[31]

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[30] Lisa Wright, 'Medieval and Early Modern Seals Under a New Light', *Digital Scholarship Lab* (blog), 20 July 2018, https://dslab.lib.rochester.edu/medieval-seals-rti/.

[31] Cultural Heritage Imaging, 'Cultural Heritage Imaging | Reflectance Transformation Imaging (RTI)', accessed 16 May 2020, http://culturalheritageimaging.org/Technologies/RTI/.

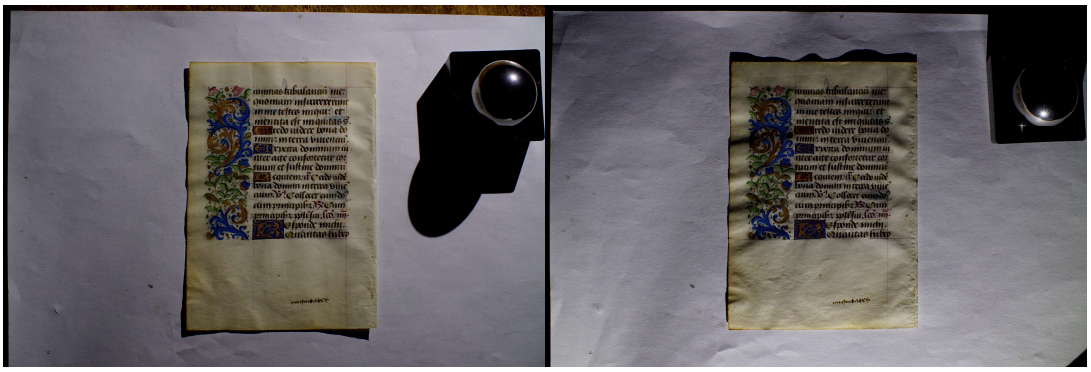

Figure 29: Two images of the same manuscript leaf taken with illumination from different angles. The shadow and the specular reflection of the ball in the top right-hand corner of each image indicate the source of the light. The manuscript leaf measures approximately 15 cm x 20 cm.

At Durham University a leaf from a fifteenth-century French manuscript was imaged with RTI. Dozens of similar images each taken from a unique angle, an example of which can be seen in Figure 29, were uploaded to the RTI software.[32] The software combines the images, utilising the specular reflection captured from a reflective ball that is also present in the images in order to ascertain illumination angle. Once processed a 3D RTI image is available for inspection and manipulation on screen. Figure 30 shows an image captured from the 3D image on the screen. The undulations of the parchment can easily be seen, as well as the textures of the ink and the paint.

Figure 30: A 2D image of a manuscript leaf captured from the 3D RTI image on the screen.[33]

[32] Cultural Heritage Imaging, 'Cultural Heritage Imaging | Process: RTIBuilder Download', accessed 16 May 2020, http://culturalheritageimaging.org/What_We_Offer/Downloads/Process/index.html.

[33] Images reproduced here with kind permission from Emilia Hepple and Joshua Dexter - Beeby Group Durham undergraduate summer placement students 2019.

Colour space L*a* b*

Theory

CIELab is a method of describing colour in numbers, which is considered to be superior to the RGB method. In CIELab, often referred to as L*a*b* or Lab, the L* quantity denotes the luminance or brightness of the image in the range 0 to 100 where 0 is black, and 100 is white. Therefore, the higher the value of L*, the brighter a colour is. The a* value measures the amount of red or green tones in an image. Although there is no definitive range for a* values, measurements typically fall between -100 and 100, with a large positive a* value meaning the colour is magenta and a large negative a* value meaning the colour is green. Similarly, the b* value also has a range between -100 and 100, but b* measures blue and yellow tones, with a large positive b* value meaning the colour is yellow, and a large negative value meaning the colour is blue.[34]

The advantage of L*a*b* colour space is that the brightness of the image can be separated from the colour of the image, meaning that with respect to a white point the measurement of colour is independent of the device used to capture the image, and the lighting of the image.

Applications

One way in which the ability to measure colour is useful is that colours can be compared. In this study of manuscripts, it can be beneficial to compare colours in different manuscripts that might be miles apart physically and, more importantly, to be able to do so objectively without relying on colour photographs and a discerning eye!

[34] 'Convert RGB to CIE 1976 L*a*b* - MATLAB Rgb2lab - MathWorks United Kingdom', accessed 23 May 2020, https://uk.mathworks.com/help/images/ref/rgb2lab.html#description.

Figure 31: The initial from NCO MS.1 fol. 401r.

Figure 31 shows an initial from NCO MS. 1 fol. 401r. In MatLab, the image can be processed to show each pixel from the in L*a*b* colour space. As there are three quantities in L*a*b* the resulting plot of pixels, called a point cloud, is necessarily 3D. The point cloud can be rotated on the screen so that all the colours can be seen - a 2D picture tries to capture two views of the 3D point cloud in Figure 32. Each pixel of the image is represented by a dot in the 3-D projection, which form clusters or clouds representing regions of similar colour. As the image analysed is predominately blue and pink, these colours make up the bulk of the cloud. There is a little green in the image, for example, meaning a small green area can be seen in the left-hand image.

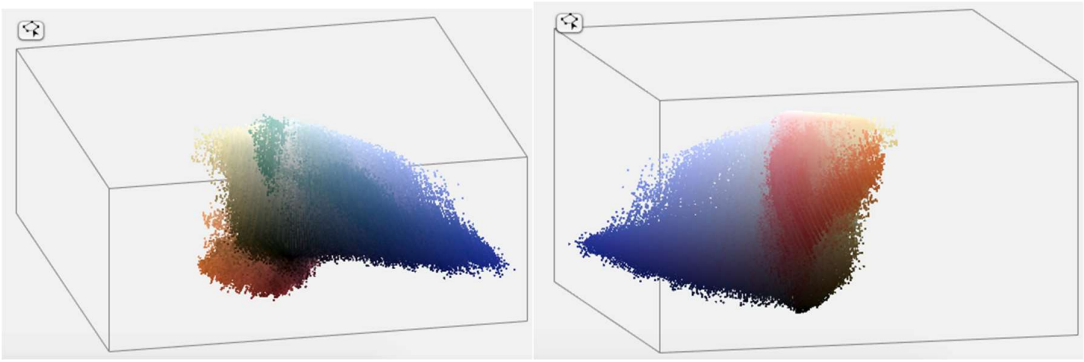

*Figure 32: Two views of the same point cloud of the pixel colours from the image in Figure 31. The axes are the L*a*b* dimensions.*

The image can be re-plotted using only pixels that fall into certain regions of L*a*b* space, allowing areas with a similar colour to be represented in the image. The 'colour threshold' tool in MATLAB's application library was used to isolate the pink colour from the image and analyse it in L*a*b*.

Figure 31 shows the full-colour image taken, whilst Figure 33 represents the image with only the pink colour remaining (the blue line is from the Matlab selection tool).

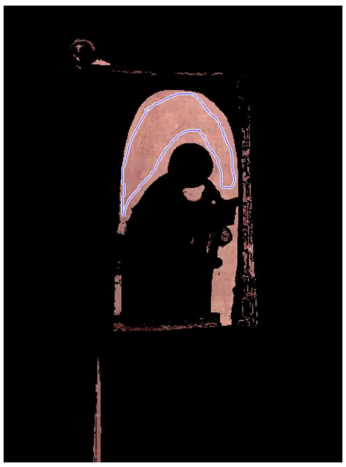

Figure 33: The initial on NCO MS 1 fol. 401r showing only the areas coloured in pink.

As can be seen in Figure 34, the point cloud now shows only the pink colours obtained from the image, and a histogram shows the number of pixels at each L*, a*, and b* value. The L* value can be set aside, as in this case it is the 'pinkness' of the colour as ascertained by the blue-yellow and red-green quantities that is of interest, not the luminescence. The a* value ranges from approximately 16 to 29 and the *b values from 8 to 18.

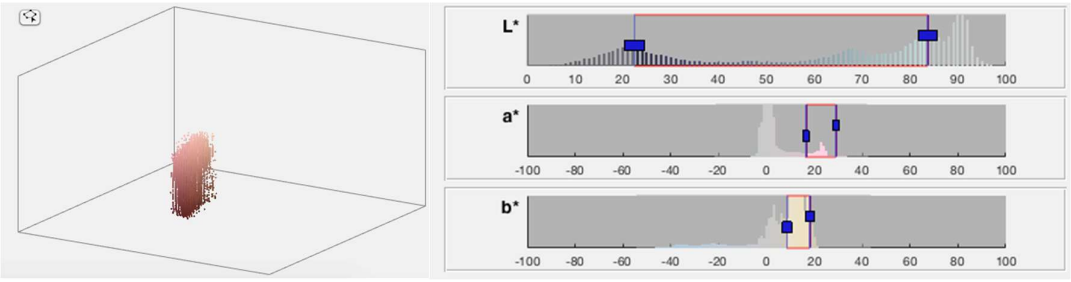

*Figure 34: (left) The pink colour in L*a*b* colourspace, and (right) the L*a*b* values of the pink pixels.*

The a*b* value of each can be plotted most meaningfully on a scatterplot, as seen in Figure 35 below. Here the range of values can easily be seen, and the midpoint of each can be ascertained. The mean of the a*b* values can also be calculated, allowing comparison between pigments which,

whilst not diagnostic, indicate whether or not they might be the same. In Chapter 4, this technique is used for the comparison of pinks and blues in seven manuscripts.

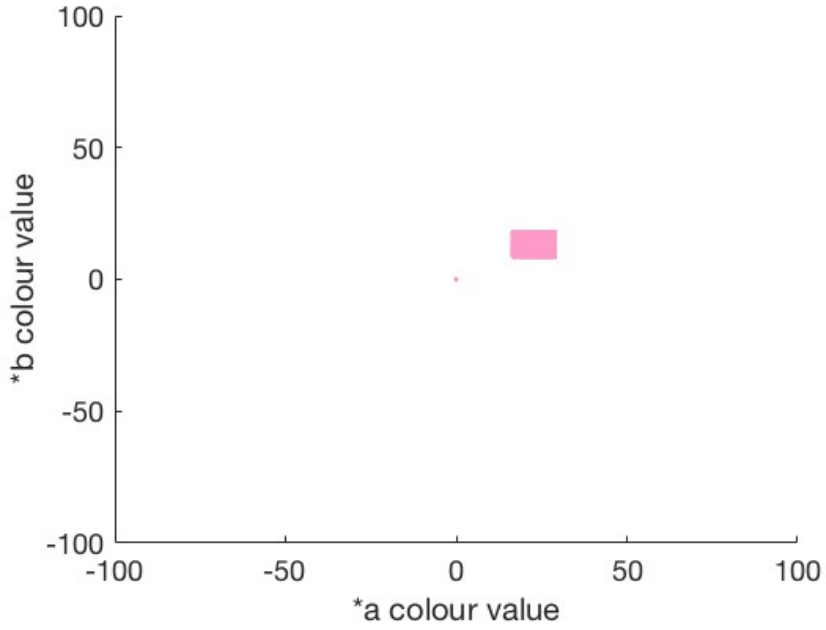

*Figure 35: A scatter plot of the *a*b values from the pink colour of the initial on fol. 401r.*

X-Ray Fluorescence

Theory

X-ray fluorescence is an elemental analysis technique that is used to ascertain which atoms are present in a sample. X-rays have wavelengths of between 0.01 - 10 nm, or 0.1 - 100 keV, and are therefore described as being from the 'high energy' part of the spectrum.

In pigment analysis, the area under analysis is irradiated with primary X-rays that are emitted from a handheld analyser. The X-rays that are directed onto the sample have sufficient energy to overcome the binding energy of an electron and dislodge or eject an electron from the inner shell of an atom (K shell). The ejected electron leaves a 'gap' that is filled by an electron from an outer shell (L or M shells).

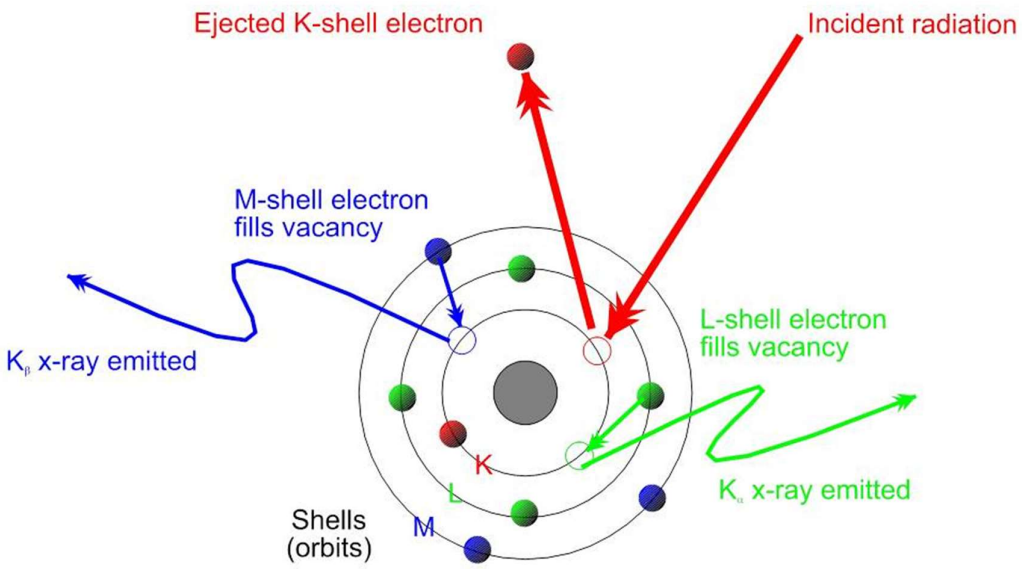

Figure 36: X-ray fluorescence diagram.[35]

It is the movement of this electron between the outer shell and the inner shell that produces secondary or fluorescence x-rays, and it is this which is measured by the analyser. As the energy released by the movement of the electrons is characteristic of the atom in which the movement takes place, the energy output can be examined, and the element ascertained.

Applications

As it is non-destructive and non-contact, XRF is appropriate for the analysis of manuscripts and other artworks, although it is best suited to analysing metals and pigments where Z >8, i.e. elements that have higher numbers of electrons - gold and mercury, rather than carbon, for example.

As the spot size of the equipment is reasonably large, it is suited to measuring larger areas that are coloured in one colour, or one metal.

[35] 'How Does XRF Work?', Bruker.com, accessed 23 May 2020, https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/handheld-xrf/how-xrf-works.html.

Figure 37: (left) JRL Lat.98 fols. 15v and 16r, and (right) the area on fol. 16r that was analysed by handheld XRF.

At the John Ryland's Library, Manchester, XRF examination took place on several manuscripts and was used, primarily, to ascertain if the gold illumination was pure gold. The manuscript and section of the page under examination can be seen in Figure 37. It is sometimes the case that gold was mixed with other metals, or that brass was employed - as has been seen as a gold substitute in a ninth-century manuscript. The results of this analysis can be seen below in Figure 38 and are discussed in the next section.

Limitations

As both the irradiating X-rays and the secondary X-rays are high energy and cause ionisation, specific legislation governs their use, and well-prescribed codes of practice exist. Therefore, XRF equipment can only be deployed by a trained operative under strict conditions with precautions in place.

Team Pigment utilised a handheld portable XRF Bruker Tracer III-V, kindly loaned on occasion by Northumbria University. It operates at 40 kV, and each reading takes 300 seconds. The area of irradiation is a 5 mm spot. In the analysis of artwork in manuscripts, this is quite a large area; thus, XRF must be considered a blunt tool, rather than a precision one, as pigments typically occupy very small areas.

Furthermore, because the X-Rays are of high energy, they can penetrate a distance of approximately 30 cm through a manuscript, meaning that any pigments in pages directly underneath the one being analysed are also included. This problem can be overcome by isolating the page in question, or by placing a shield behind the target page, but is something that must be considered. In addition, the results from XRF need careful interpretation. Figure 38 shows the results from the examination of JRL Lat. 98 fol. 16 r. As can be seen, in the area analysed there are 140,000 parts per million of gold, accounting for over 99% of the sample, with some lead, calcium, and copper detected as well before the results start to show trace and ultra-trace elements. These results confirm that the golden area is indeed gold metal. The copper, lead, and calcium readings can be attributed to the red lead and white lead found in this manuscript, as well as copper green. The calcium reading is possibly from the chalk or limestone used to prepare the parchment.

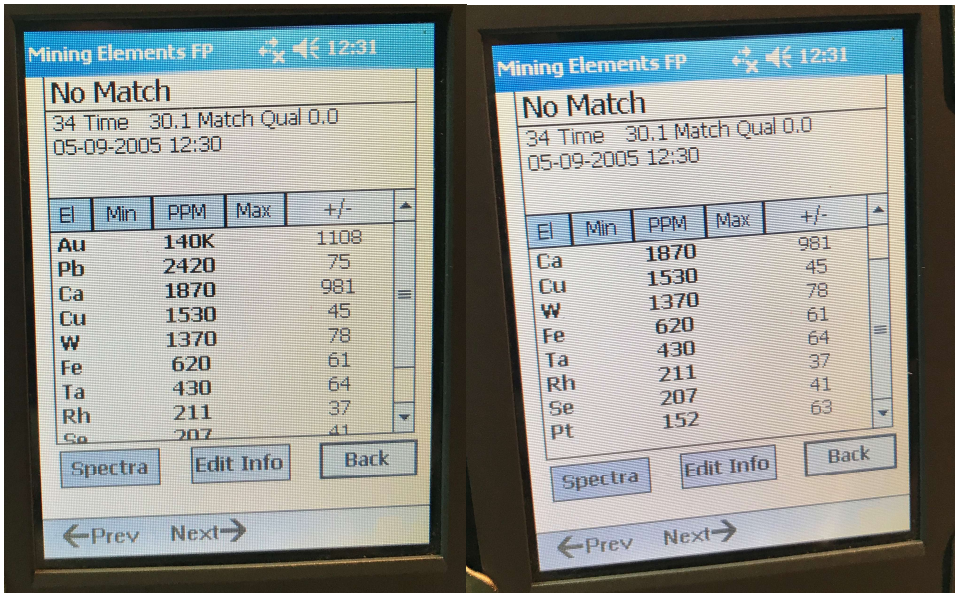

Figure 38: The results from XRF analysis on JRL Lat. 98 fol. 16 r.

Conclusion

This chapter has discussed the theory, applications and limitations of several spectroscopic techniques that have been utilised in the analysis of artworks in manuscripts. FORS, both in the visible and near infrared, is a powerful tool for analysis of both mineral pigments and dyes but has limitations particularly for the examination of organic substances. Raman spectroscopy can give a conclusive result for many mineral pigments, but again, the examination of organic substances can prove problematic. Imaging techniques, including multispectral imaging and its applications, microscopy, and RTI can all add significant evidence to pigment and artwork examination, whilst XRF is a useful tool, particularly for metal analysis. Computer-based evaluation of colour can provide additional information for colour comparison, although it is not diagnostic in identification.

It is clear that for a thorough examination of a manuscript, all of these techniques should be used in conjunction. Furthermore, it is imperative that the equipment employed is optimised for working with priceless manuscripts, i.e. that the equipment used is non-invasive and non-contact.

Protocol

With these advantages and limitations in mind it becomes possible to design a protocol of scientific manuscript analysis to ensure safe and smooth operation of equipment whilst gathering the maximum information available in the time allowed.

Firstly, even before the examination begins, it is prudent to have in mind questions one wants answered about the colourants in the manuscript, and to have researched the date and provenance of the manuscript, as a minimum. The questions that one might have about a manuscript could be very broad - what pigments were available to an artist creating a manuscript in eleventh century Oxford, for example, or they may be very targeted - how did different artists deploy blue pigments to create shading in the artwork of the second half of this manuscript, perhaps.

In turn, these questions inform the setup of equipment. If only under-drawings are to be examined, then obviously only the multispectral imaging equipment will be set up. However, presuming that a full-scale investigation is required, then it is pertinent to run a quick "triage" with a handheld infrared camera over the manuscript. This will give very quick real-time information as to the potential areas of carbon and azurite in the manuscript, as these pigments will appear dark on the infrared camera. This may in turn inform the decision as to whether to continue the analysis with Raman spectroscopy or FORS next.

Following the set-up of the equipment, the laser and/or FORS beam are checked with a power meter to ensure that the power density that the manuscript receives is less than 0.5 $mWcm^{-2}$. This check is repeated several times during examination, particularly after breaks, or when the equipment has been running for a while. After investigation with either Raman spectroscopy of FORS, the other method is then used to confirm identification where achievable. It is possible to see and identify instantly the spectra for some pigments - e.g., the vermilion and orpiment signals on the Raman spectrometer are unmistakable, and the flat signal from carbon when FORS is used is also obvious. However, sometimes the spectra require processing later (background removal for Raman spectra and KM transformation for FORS) in order to reveal signature peaks, absorbance maxima or inflection points.

Following execution of these standard methods the data obtained may raise further questions, and after Raman and FORS examination it may be prudent to redo certain areas again, or to use XRF, or microscopy at this point.

Lastly, multispectral images of each page examined, and possibly other pages, are taken. This allows for accurate pin-pointing of the spots examined at a later date but can also provide a confirmation to identification of the pigments - e.g., carbon and azurite in the IR. Processing the images can produce revealing false colour images as descried above. If RTI would be helpful, then this would also be performed this point, with the images processed later.

After examination and disassembly of the equipment then computer-based analysis can begin. Each manuscripts raw data and processed data is recorded by country, city or town, library and shelfmark, and then the data from each fol. examined is recorded within by technique. Information from the computer system for the day, such as Raman background and FORS dark and white spectra are also recorded, in case of any problems. Any images taken besides the multispectral images are also saved.

Chapter Four Part A

Introduction

Analysis of DCL A.II.3 and DUL Cosin V.v.17

Introduction

Bibles in the Thirteenth Century

The thirteenth century was a period of innovation in the form and function of the bible. It changed from a book that was large and unwieldy, primarily owned and used only by religious houses and their communities to a portable book possessed by individuals. That is not to say that every bible produced then and henceforth was for individual use, be it for student, friar, or priest, as production of large-format bibles continued. However, the sheer number of portable thirteenth-century bibles that exist today tells us something of the scale of production of this new style of bible.[1]

This change in practice was linked to other important changes in bible production – the typical form became the pandect, and a new, smaller, format was adopted. These changes, in turn, were made possible by developing a new technology to produce thinner parchment.[2]

In the early decades of the century, a new type of bible text was developed, and this was copied profusely in Northern France, in particular Paris, which lent its name to the new format. However, the term 'Paris Bible' is a misnomer in that it refers to a type of text rather than necessarily to the place of creation. Simultaneously, one particular system for dividing the books into chapters, which had originated in the middle of the twelfth century and is ostensibly the same at that used today, was adopted wholesale.[3]

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[1]Laura Light, 'The thirteenth century and the Paris Bible' in Eyal Poleg and Laura Light, eds., *Form and Function in the Late Medieval Bible*, Library of the Written Word, Vol. 27 (Leiden ; Boston: Brill, 2013), p. 380; Richard Gameson et al., *Manuscript Treasures of Durham Cathedral*, 2010, p. 104.

[2] Sarah Fiddyment et al., 'Animal Origin of 13th-Century Uterine Vellum Revealed Using Noninvasive Peptide Fingerprinting', *Proceedings of the National Academy of Sciences* 112, no. 49 (8 December 2015), p.1.

[3] Poleg and Light, *Form and Function in the Late Medieval Bible*, p. 385.

Paris Bibles

The development of the Paris Bible text type was the result of two phases of change in the order and standardisation of the text. The first stage, which occurred around 1200, was a re-ordering and refining of the books of the bible to what is essentially the modern Vulgate. IV Ezra, for example, was removed, whilst Baruch was included, and sixty-four prologues were added. In the second phase, around 1230, the prologues were adjusted, the capitula lists replaced with standardised chapter divisions and a list of Hebrew names appended.[4]

Keenly copied in Paris during the thirteenth century, it seems that the Paris Bible was imitated elsewhere in France and Europe, certainly in Italy and England, whilst its style, particularly the order of books, influenced bibles being copied in Germany and Spain.

Rationale

This study examines seven Paris Bibles, from Durham Cathedral Library, Durham University Library and New College, Oxford. They form a small but representative sample of the approximately one thousand Paris Bibles from the thirteenth century that survive today. The bibles are representative as those examined are predominately pocket-sized, but include one large example, which reflects the trend of the time – of 642 bibles surveyed in 1960, 420 were less than 200 mm in height.[5] In addition, most of the bibles examined are thought to have been made in Paris, but two were made in Southern England, again, reflecting the origin of the manuscripts made at this time.

In addition, one bible gloss from New College, Oxford, was also examined, to provide comparandum to the one English Paris style bible examined, and to add further context to the discussion of pigments in thirteenth-century Northern Europe in general.

Investigation into the similarities and differences of pigment use and artistic technique in the specimen bibles will further inform scholarship that seeks to understand how these volumes were made, what pigments were available and commonly used in Paris and Southern England at this time, and how they were deployed.

[4] Poleg and Light, p. 384.

[5] Light in 'Poleg and Light, p. 381.'

Manuscripts examined

Durham University

Durham University holds two pocket-sized Paris Bibles – Cosin V.V.17 and Cosin V.V.18. Both are part of Bishop Cosin's Library, founded in 1669 as an endowed library by John Cosin, Bishop of Durham from 1660 to 1672.

Durham Cathedral Library

Durham Cathedral holds three Paris Bibles – A.II.3, A.IV.30 and A.IV.37. A.II.3, which has been described as 'A luxurious French Gothic Bible', is certainly a very fine manuscript and is one of the jewels in the crown of the cathedral collection, where it has been since at least 1395, as it is listed in the Durham Priory Library catalogue of that date.[6] It is certainly not a pocket-sized bible, although nor is it a 'giant' bible. The other two bibles are pocket-sized.

New College, Oxford

Two biblical texts were examined in situ at New College Oxford MS. 1 and MS. 20. MS. 1 is a Paris Bible, thought to have been made in Paris. It is not pocket-sized but is portable. MS. 20 is a Biblical gloss made in Southern England. It too is not pocket-sized - a biblical gloss would have been used for study and not personal worship, so it would be unusual for a gloss to have been made with portability in mind.

Technical Details

As detailed fully in chapter three, colourants were examined where possible with both VIS-NIR FORS and Raman spectroscopy, with additional information gleaned from microscopy, multispectral imaging, and colour analysis.

[6] Gameson et al., *Manuscript Treasures of Durham Cathedral*, p. 107.

Durham Cathedral Library A.II.3

Description and Provenance

One of the finest manuscripts in Durham Cathedral's collection is a handsomely decorated bible, A.II.3. Measuring 412 mm by 272 mm, the book was designed for the lectern rather than the pocket. It contains the Bible text in Latin (fols. 2r to 415v) followed by the Dictionary of Hebrew names (fols. 417r to 452r). Several features of this manuscript place it in the Paris Bible tradition as outlined above – the order of the books of the bible, the set of prologues prefacing them, the system of chapter divisions and the inclusion of the list of Hebrew names. Furthermore, the script (textualis semi-quadrata), the artwork, and the pen flourishing indicate Paris as the place of creation of the manuscript and point to a date in the second half of the thirteenth century.[7]

Codicology

Quire Formation

Aside from a few aberrations, discussed below, the quires usually comprise six sheets (bifolia) folded to make a twelve-leaf gathering.

Parchment and Ruling

The parchment is of good quality but is now generally weathered and has signs of use. The folios are arranged flesh side facing flesh side and hair side to hair side, as is usual. The parchment was pricked with an awl or knife (some prickings survive in the upper and lower margins). The folios are ruled in two columns.

[7] Gameson et al., p. 107; Poleg and Light, *Form and Function in the Late Medieval Bible*, p. 388.

Figure 1: DCL A.II.3 fol. 217 showing the cut out section.

Despoliation

As discussed below, folio 3 is displaced, and the original folio 1 is missing. There is some liquid damage to the outer edge of many leaves, and a few leaves are very dirty. There is a V-shaped area missing from fol. 217, shown in Figure 1. The initial on fol. 135v denoting the book of Paralipomenon (Chronicles) has been excised.

Figure 2: Fol. 10r showing two columns of text, and two text initials and their accompanying line of red and blue waterfalls. A correction can be seen in the right margin.

Layout, Ornamentation and Rubrics

Each page contains two columns of text with 54 lines of writing, with each column measuring 77 mm wide and 269 mm high. The ruled lines are 5 mm apart, and the written minims are typically 3 mm high. Historiated initials head the preface to each book of the bible, and the individual books themselves also have an historiated initial. The letter outline of these is typically 8 lines high, enhanced by decorative extensions that run the length of the page. The letters and contain figural scenes within them, which depict some aspect of the text that follows.

Chapter initials are red and blue and are flourished in contrasting red or blue; a line of alternating red and blue waterfalls, the length of the column, accompanies each text initial. This means that a given page can have no waterfalls, one column of waterfalls or even two, as seen in Figure 2. Chapter numbers are written in red and blue Roman numerals preceding each chapter initial, and the running headings (giving book name and chapter number) of the chapters are also in alternating red and blue at the top of the page, also seen in Figure 2.

Script and Hands

The text is a neat, regular, textualis semi-quadrata in a rich black ink, probably by a single hand. Sentence capitals are stroked in red. Corrections were made in the margins, by the original scribe and then boxed in red and flourished in blue.

Artwork

Artists and Painters

The style of the faces drawn throughout the book, with their pear-shaped heads and brief yet deft features, suggests the work of one drafting artist. However, from the slightly differing palettes, as described further below, it seems that two painters were responsible for the colouration of the figures, one working from the beginning of the manuscript to 228v and the other from 229r to the end of the book. Fol. 229r is the start of a new quire, and occurring roughly half-way through the book, suggesting that the division of painting was made to expedite production – rather than for aesthetic or personnel reasons. Hereafter I shall refer to the two painters as Painter One and Painter Two, and their respective parts of the book as Section One and Section Two. One curiosity of the book is that fol. 2r, the first page after the fly-leaf - which is the preface to Jerome, seems to have been painted by Painter Two rather than Painter One as might have been expected.

Another painter/artist likely accomplished the ornamentation of the text – the running headings, the chapter initials, the flourishing around the corrections, and probably the index as well.

Style of Artwork

As is usual for the genre, the figures in the historiated initials represent a key person or scene from the text to come. They are depicted in front of a coloured 'tiled' background, rather than a setting, with only a few props to convey the scene, which can seem repetitive at times. The pear shape of the head of the figures in this manuscript, and the nature of the facial features, summarily but skilfully indicated, has been linked to the house style of the so-called Bari Atelier in Paris, as defined by Robert Branner.[8]

[8] Robert Branner, *Manuscript Painting in Paris during the Reign of Saint Louis: A Study of Styles*, California Studies in the History of Art 18 (Berkeley: University of California Press, 1977), p. 102; Gameson et al., *Manuscript Treasures of Durham Cathedral*, p. 107.

However, Branner's classification of the place of manuscript manufacture purely on stylistic grounds can be problematic. Artists were not confined to one style and atelier during their careers, so may have moved to different atelier taking their skills and their styles with them, ready to replicate what they had done at another atelier. Furthermore, it is known that exemplar copy books of artwork and text styles were circulating ateliers at this time, and it would not be difficult to imagine these influencing the artists to try different styles, inspired by those seen in the exemplars.[9] In addition, patron taste must surely have had some influence on the style and colouring of the artwork produced. Using one style as a definitive classification of production at one atelier must be taken as a suggestion rather than as fact.

Approach to Painting

The devil, which features on the first folio of the book, is painted in a different, more sophisticated style than the rest of the artwork, with many different tones being used for his skin and with highlights to create texture and detail, as seen in Figure 3. The attention to detail is impressive: the nipples are highlighted in white to bring out the brown centre, and the thinnest of white lines used to emphasise form. It is probably due to its position as the first page in the book that the interesting subject matter was treated to such a masterly application of paint. The incipit to Genesis, which would normally be the first page of the bible proper, was excised leaving only a stub. This is because it would likely have been one of the most splendid pages of the book.[10]

[9] Christopher De Hamel, *Scribes and Illuminators*, Medieval Craftsmen (Toronto ; Buffalo: University of Toronto Press, 1992), p. 35.

[10] Richard Gameson, "Durham's Paris Bible" in Poleg and Light, *Form and Function in the Late Medieval Bible*, p. 69.

Figure 3: The Devil, from the General Preface of Jerome, DCL A.II.3 fol. 2r.

The rest of the manuscript is painted in a simpler, more formulaic style whichever artist was responsible. Faces, for example, are given the same treatment by both artists. As seen in Figure 4, the faces from Paralipomenon (fol. 146v) and Matthew (fol. 401r) are very similar, despite being painted by different hands. All of them are white and have features outlined in black with delicate highlighting in cream around the nose and eyebrows. The lips have been accentuated with a touch of red (more so those of female personalities), whilst Mary's cheeks are even given a blush of red. Blue has been used to provide contour. Hair is given brief but confident attention – a few strokes of the pen delineate both straight and curly hair, female and male alike. The size of these faces in the manuscript is probably only 1 cm^2, so far from criticising the summary nature of the artwork, one has to marvel at the attention to detail given to such tiny areas.

Figure 4: Microscopy images of faces from Paralipomenon on fol. 146v (left) by Painter One, and (centre and right) from Matthew on fol. 340r by Painter Two.

One difference between Section One and Section Two of the book that is not immediately noticeable to the eye, but that becomes more apparent when analysed with multispectral imaging, is that the painters employed differing techniques to render the backgrounds to the scenes.

Figure 5: (left) A photomicrograph of DCL A.II.3 fol. 100v, and (right) a section of fol. 259 v.

In the left-hand image of Figure 5, the blue checkered background is delineated with black lines, and overpainted with diagonal white lines and white and orange circles - these would have been done by Painter One. However, as seen in the righthand image of Figure 5, Painter Two's black lines are much less noticeable, making the white diagonal lines more apparent. Though evident when highlighted thus via IR, such differences will have been less apparent to a reader leafing through the volume.

Indeed, had it not been for the infrared images ($\lambda > 800$ nm) seen below in Figure 6, it is possible that these differences may have been missed. However, when viewed in this way, the differences are stark. Painter One's thick black carbon lines are impossible to miss (and the fact that they do not continue

under or through the figures suggests the lines were painted in subsequently), whilst Painter Two's lines are barely visible.

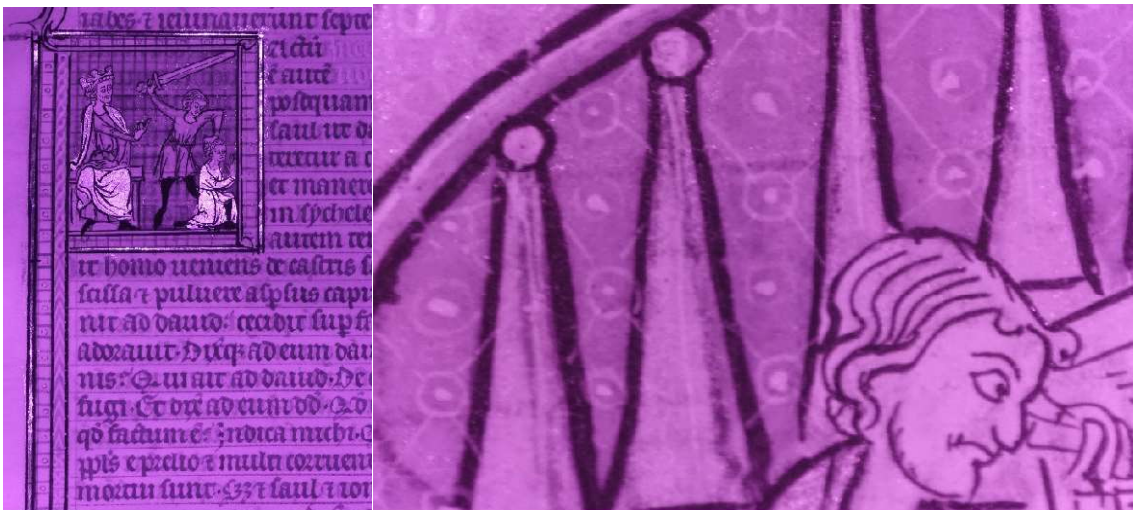


Figure 6: (left) A section DCL A.II.3 fol. 100v under IR illumination, and (right) a section of fol. 259v under IR illumination.

Figure 7: The ultraviolet image of a section of the illumination on DCL A.II.3 fol. 259v, showing underdrawings that guided the colouring artist.

Underdrawings, recovered with the help of multispectral imaging (particularly those recovered in the NIR), guided the artwork with regard to size and content, as can be seen in Figure 7, where the underdrawings of the lines to guide the position of the curl can be seen. These sketches were not always strictly adhered to, as is clear from Figure 8, where the painter has changed the length of the knife and the positioning of the quill.

Figure 8: (left) An image of DCL A.II.3 fol. 2r taken under IR illumination, and (right) the same area under white light.

Figure 9 highlights an important revision that occurred between the design stage and the application of paint, the painter correctly supplying an 'A' instead of the 'S' that had been erroneously sketched by the designer. The two New Testament books that could begin with an 'S' are II Peter and III John, which are often close to the book of the Apocalypse (there was still some flexibility in the ordering of the New Testament books at this time), so it seems likely that originally one of these books was intended, the order of the books changing from the initial plan.

Figure 9: (left) The initial on A.II.3 fol. 409r under white light, (centre) the same initial under IR light showing the under drawing and (right) the same image with the under drawn 'S' marked for clarity.

Figure 10: A photomicrograph of part of the artwork on DCL A.II.3 fol. 259v (left) under overhead illumination and, (right) under raked illumination.

In Figure 10 above, the image taken under oblique illumination allows some conclusions to be drawn about the orders in which the paints were applied. It is clear from the overlaying of paint that the pale pink background is painted over with darker red lines, to which white and orange detailing is then added. Although the undulations of the parchment in the oblique image make it difficult to be sure, it does appear that the figure is painted on top of the already completed darker pink lines, which suggests that some of the background was already painted when the figure was added. However, the gap between the orange halo and the pink background, towards the left of the image, suggests the opposite – that the background was added afterwards. The ultraviolet image shown in Figure 11, does not yield any further clues as to the order of paint application.

Figure 11: A photomicrograph of a section of DCL A.II.3 fol. 259v taken under ultraviolet illumination.

Palette

In this section, the palette and pigments used by the artists of the decorated initials is discussed. The colour choice and pigments used for the text ornamentation – running headings, text initials and corrections etc. are discussed separately because, as previously mentioned, these were likely done by a different hand.

Throughout the manuscript, saturated blues and a strong pink are complimented with a dusky pink, a vivid orange, white, black, a blueish-grey, a vibrant green, and gold. These colours either stand-alone or are modified by the use of carbon to darken or white lead to lighten. With the exception of green, all the colours are typified in the painting shown in Figure 12.

The backgrounds of many of the paintings are blue and/or pink and are often modulated with orange detail which, when combined with modulation from the black and the white, gives the impression of a wider palette than is actually used. In Figure 12, the pink background is modulated with orange and white with black ruled squares around, giving the impression of different pinks when, in fact, only one is deployed. The same approach can be seen in the blue background.

Figure 12: (left) The historiated initial at the start of the book of Judges in DCL A.II.3, with an enlargement of the background.

Use of Grey

A.II.3 contains several uses of grey that are eye-catching, especially when contrasted with the saturated hues of the dark blue and the darker and dusky pinks. This grey, as seen in Figure 12 and Figure 13, is lapis ash, a by-product of the manufacturing process of lapis lazuli (discussed earlier in chapter two). It is used often throughout the book, seemingly by both artists, and modulated by carbon lines to give a darker colour.

Figure 13: (left) The historiated initial to Kings III fol. 110r.

However, whereas artist one uses only lapis ash, the second artist also uses carbon for grey, as seen in Figure 14, and indigo also, as seen in Figure 15. The use of carbon for grey on fol. 2r is interesting, as it is the only instance of carbon deployed as a colour in its own right that was seen in the pages examined. Perhaps the despised figure of the devil was considered too hateful to merit the more expensive pigments of lapis ash and indigo, or perhaps the darker tones of carbon were chosen to give a more sinister aesthetic effect.

Figure 14: The Devil, from the General Preface of Jerome, fol. 2r.

Figure 15: The historiated initial from fol. 409r, showing an indigo grey in the left-hand tower.

Indigo, not often seen in the book, is perhaps deployed to provide a contrast in colour to the other towers, as seen in Figure 15.

Spectra

Carbon

Raman spectra taken from the spot on the devil's knee, gave the signal of amorphous carbon, superimposed upon a broad fluorescent base, as shown in Figure 16. When the background is removed, the peaks at 1366 and 1590 cm^{-1} become clearer. These are consistent with published data for carbon black that state that the peaks are at 1361 and 1581 cms^{-1}.[11] The peaks in carbon can change

[11] G. Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', *Analytical Methods* 10, no. 10 (2018), p. 1222.

depending on the degree of crystallinity of the sample, which is why these peaks are different from those mentioned on p.82, for example.

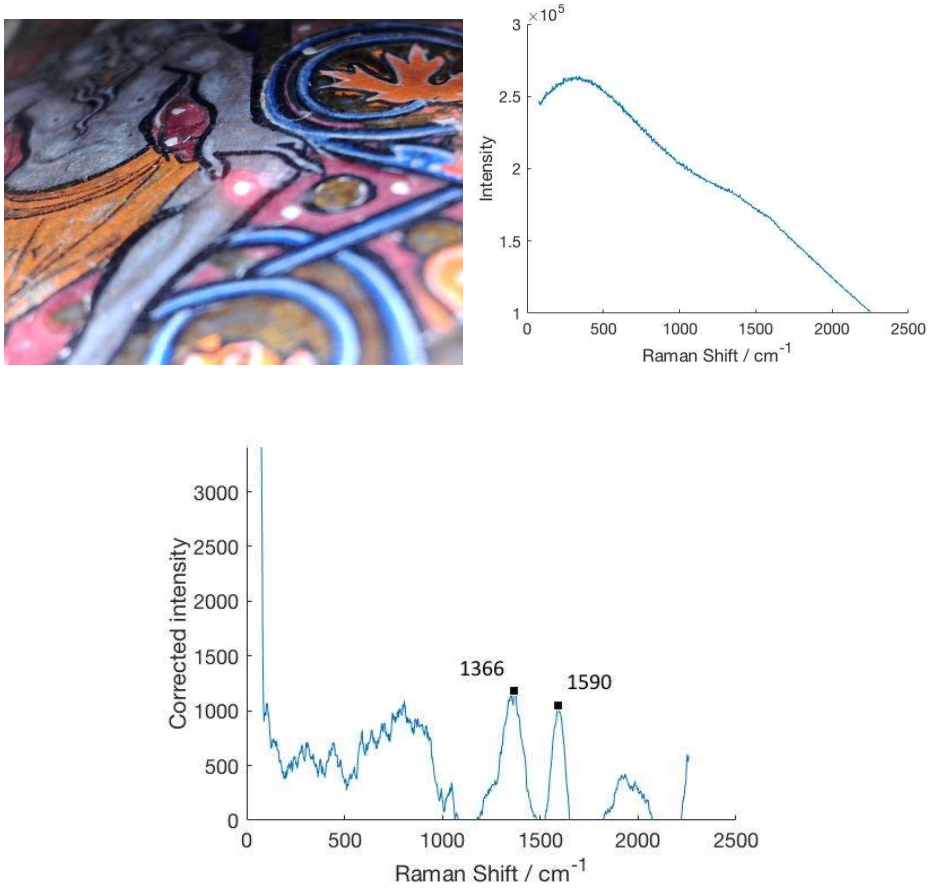


Figure 16: (top left) The spot on the grey devil's knee on fol. 2r where the Raman spectrum of carbon was obtained (top right) the raw Raman spectrum and (bottom) the spectrum after processing and background removal.

Lapis Ash

Figure 17: (right) The historiated initial at the start of Judges on fol. 76v.

Figure 17 shows the initial on fol. 76v, where a lapis ash cloak provides a contrast to the vibrant blue cloak. As Figure 18 evidences, there are clear peaks at 550 and 1098 cm^{-1}. This is lapis ash, consistent with published library data, which report peaks for lapis lazuli at 545 and 1096 cm^{-1}.

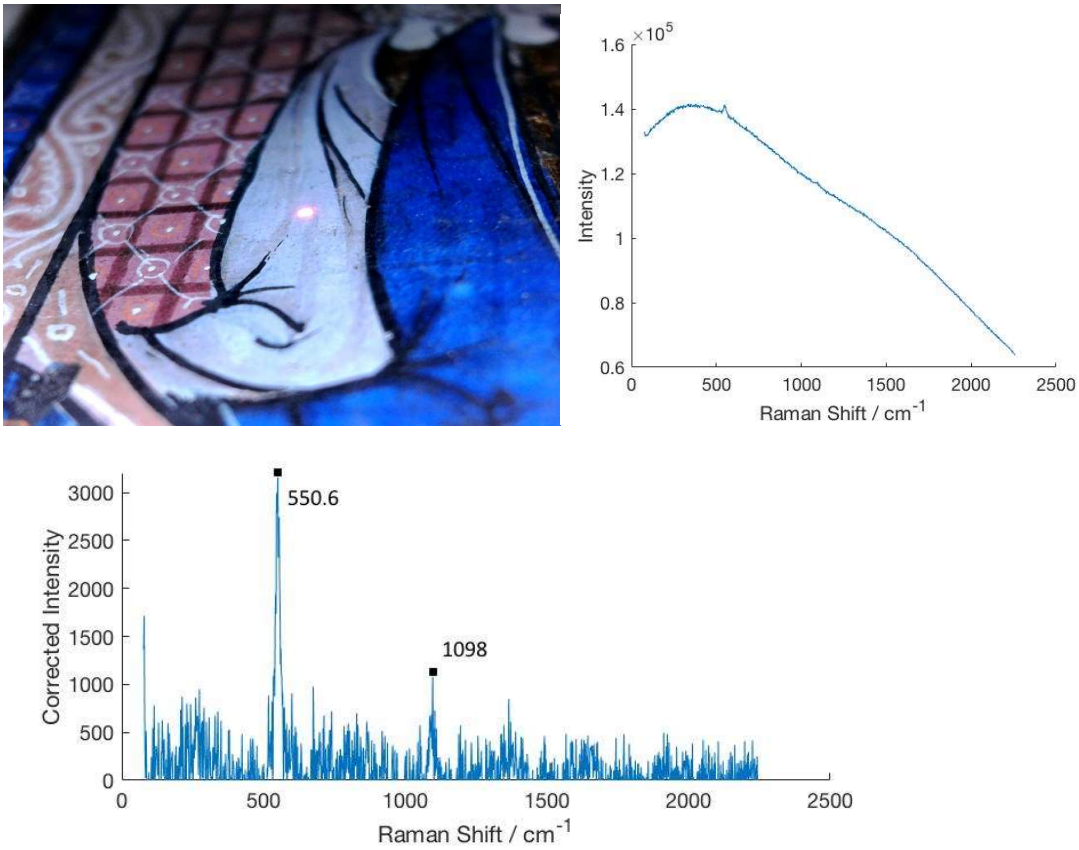


Figure 18: (top left) The spot on the grey cloak where the Raman signal was taken, (top right) the raw Raman spectra of lapis ash (the same as that of lapis lazuli), and (bottom) the processed spectrum.

Indigo

The left-hand tower of the historiations for the Apocalypse, as seen in Figure 15, features a blueish-grey that is rendered in indigo. Figure 19 indicates the area examined and the spectra obtained. By removing the background, the indigo peaks at 1590, 603, 550 and 264 cms^{-1} can be seen, consistent with the peaks given in published library data at 1578, 596, 545 and 250 cms^{-1}.[12] The extremely broad

[12] Marucci et al., p. 1222.

band to the right-hand-side of the indigo spectrum, centred around 1750 cm^{-1}, is fluorescence, which is also characteristic of indigo when excited at 633 nm.

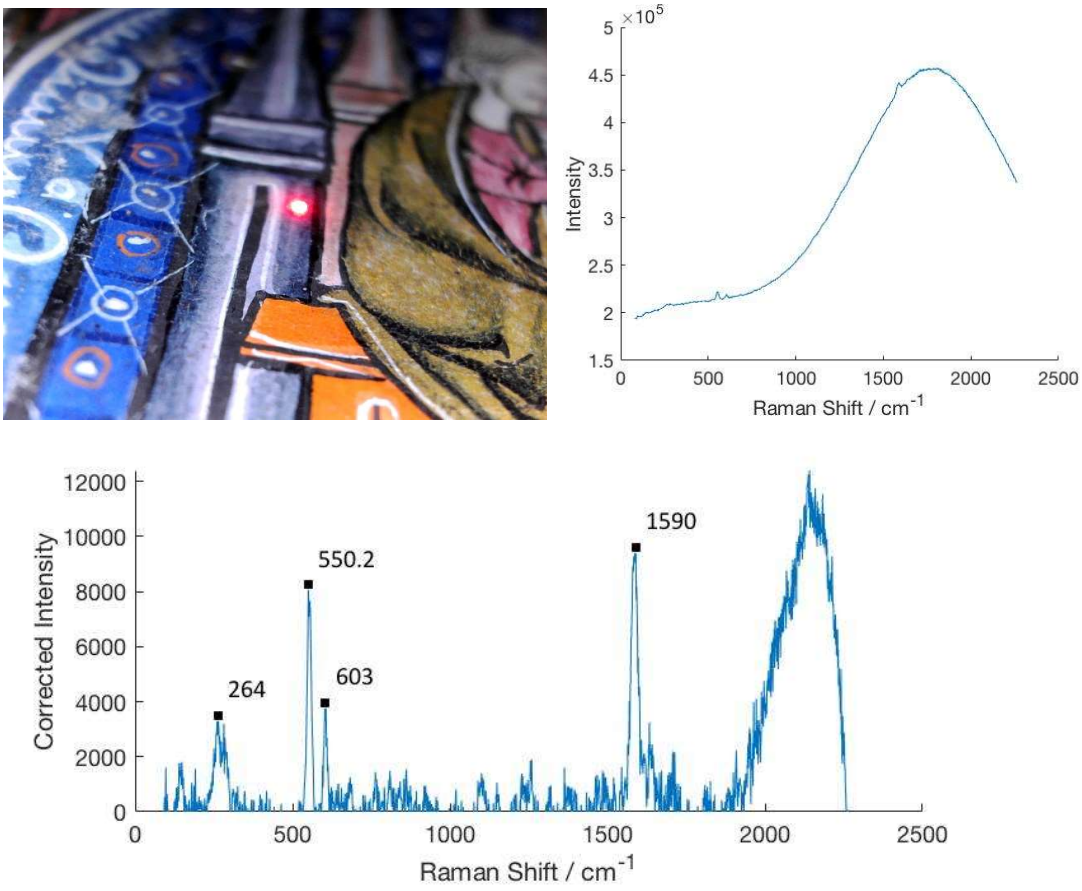


Figure 19: (top left) The spot on fol. 409r where the Raman spectrum was taken, (top right), the raw Raman spectrum obtained, and (bottom) the processed spectrum.

Figure 20: (left) A colour photomicrograph taken under white illumination of a section of draped clothing on DCL A.II.3 fol. 239v, and (right) the same section under 950 nm infrared illumination.

As can be seen in Figure 20, the drapery of the clothing (which is outlined in carbon) is shaded with a blue pigment that is transparent under IR illumination, likely to be indigo.

Use of Gold

Figure 21: (left) Fol. 68v showing Joshua, and (right) fol. 299v, depicting Daniel and the lions.

The two hands in A.II.3 use gold in differing ways. Both use gold metal to decorate both the structure of the initial and the motifs that extend into the border of the page, as seen in Figure 21. The first hand also uses gold for blocks of colour within the figural vignettes themselves. Thus, gold is used for God's halo and for Joshua's clothes and hat.

Where the first artist uses gold metal, be it leaf or paint, for the blocks of colour, the second prefers mosaic gold. As discussed in chapter two, mosaic gold is a synthetic gold pigment that, when fresh, would no doubt have looked very similar to real gold. However, the passage of time has dulled the sheen of this pigment, and it is now a murky mustard colour, as seen in the bedding of the initial to St. Matthew's Gospel shown in Figure 22. In reproductions the distinction in colour and tone is muted; viewed in the manuscript itself, however, it clearly lacks the gleam and lustre that the gold metal displays.

Figure 22: Fol. 340r, depicting Matthew lying in a mosaic gold blanket.

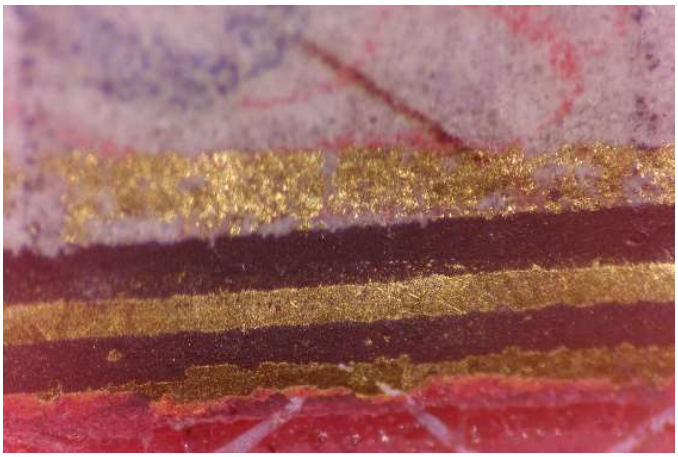


Figure 23: A photomicrograph of the gold border surrounding St. Matthew on fol. 340 r.

As seen in Figure 23, the microscope image of a border shows that gold leaf was used. It is not easy to discern the order in which the pigments were applied here: it would be usual for the black lines outlining the gold to be applied after the gold, but the image above seems to suggest the gold was applied after the black and red pigment as it sits on top of them.

Spectra

Gold Metal

Metallic gold does not give a Raman spectrum: this is evidenced in Figure 24, where a broad featureless band is returned by the spectrometer.

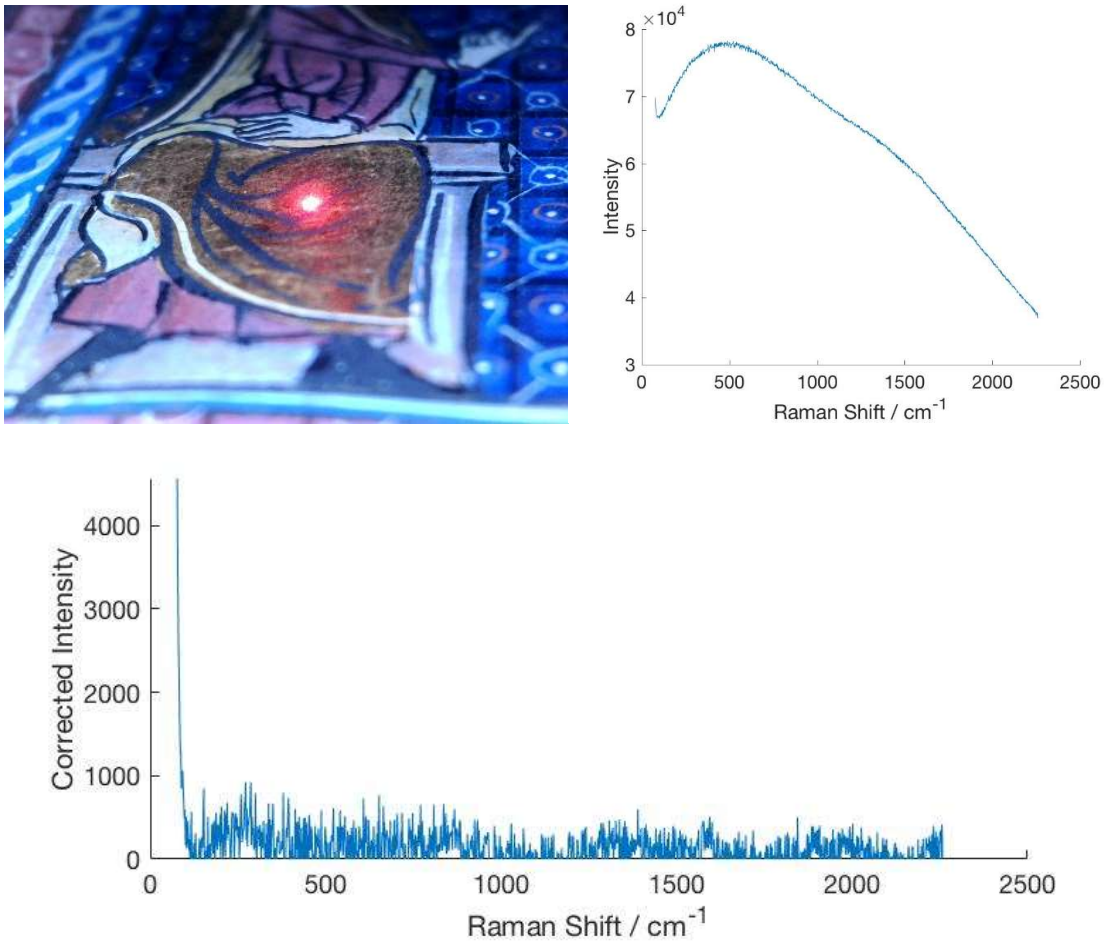


Figure 24: (top left) The spot on fol. 100v examined by Raman spectroscopy, (top right) the raw Raman spectrum of gold obtained, and (right) the corrected spectrum.

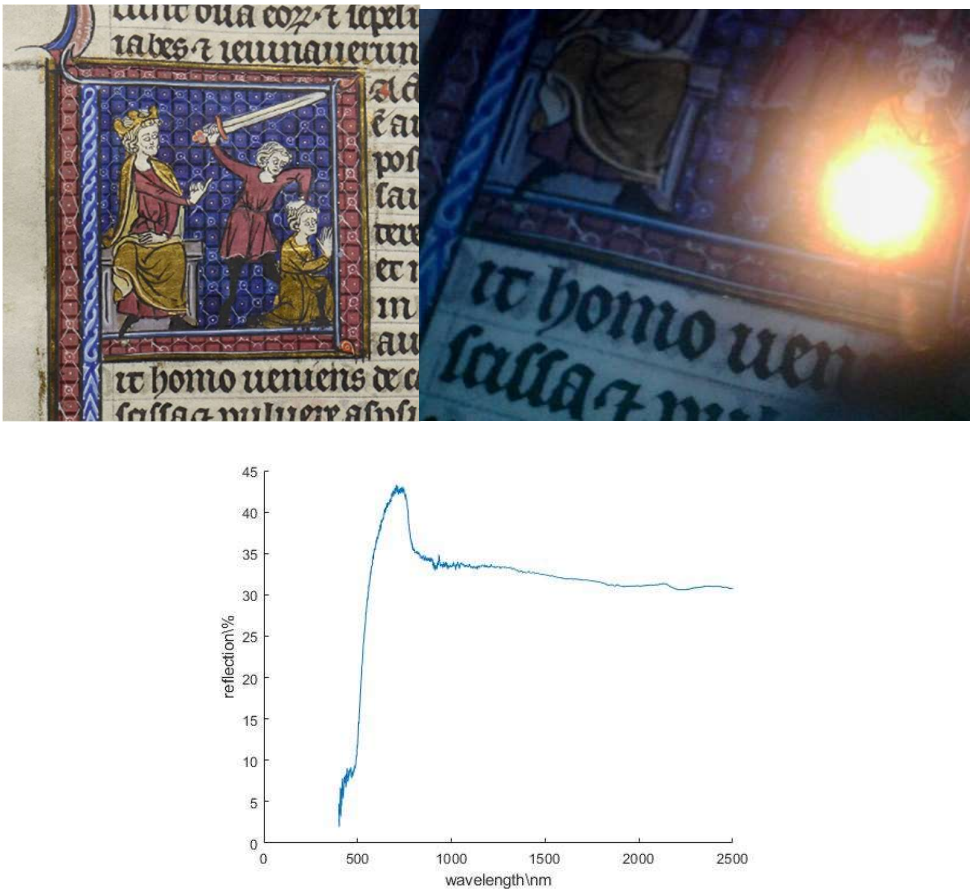


Figure 25: (top left) The historiated initial on fol. 100v (Kings I), (top right) the spot where the FORS spectra were taken, and (bottom) the spot where the FORS spectrum was obtained.

The FORS spectrum of gold is often difficult to obtain due to specular reflection. However, as seen in Figure 25, in this case a spectrum was obtained that is entirely consistent with that in published library data, which state there is an inflection point at 510 nm. In addition, because the layers of gold are so optically dense, no trace of underlying bole or gesso, or the underlying parchment, can be seen.[13]

[13] Maurizio Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', *Analytical Methods* 6, no. 5 (2014), p.1491.

Mosaic Gold

Figure 26: The historiated initial on fol. 340r (Mathew).

As shown in Figure 26, the historiated initial on fol. 340r displays the murky gold colour that colours the bedding. When examined, this colourant was found to be mosaic gold. The Raman spectrum of mosaic gold, as seen in Figure 27, with a peak at 317 cm^{-1}, is entirely consistent with published library data, which state that the Raman spectrum of mosaic gold (tin (IV) sulfide) has a peak at 314 cm^{-1}.[14]

[14] Lucia Burgio and Robin J.H Clark, 'Library of FT-Raman Spectra of Pigments, Minerals, Pigment Media and Varnishes, and Supplement to Existing Library of Raman Spectra of Pigments with Visible Excitation', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 57, no. 7 (June 2001): 1491–1521.

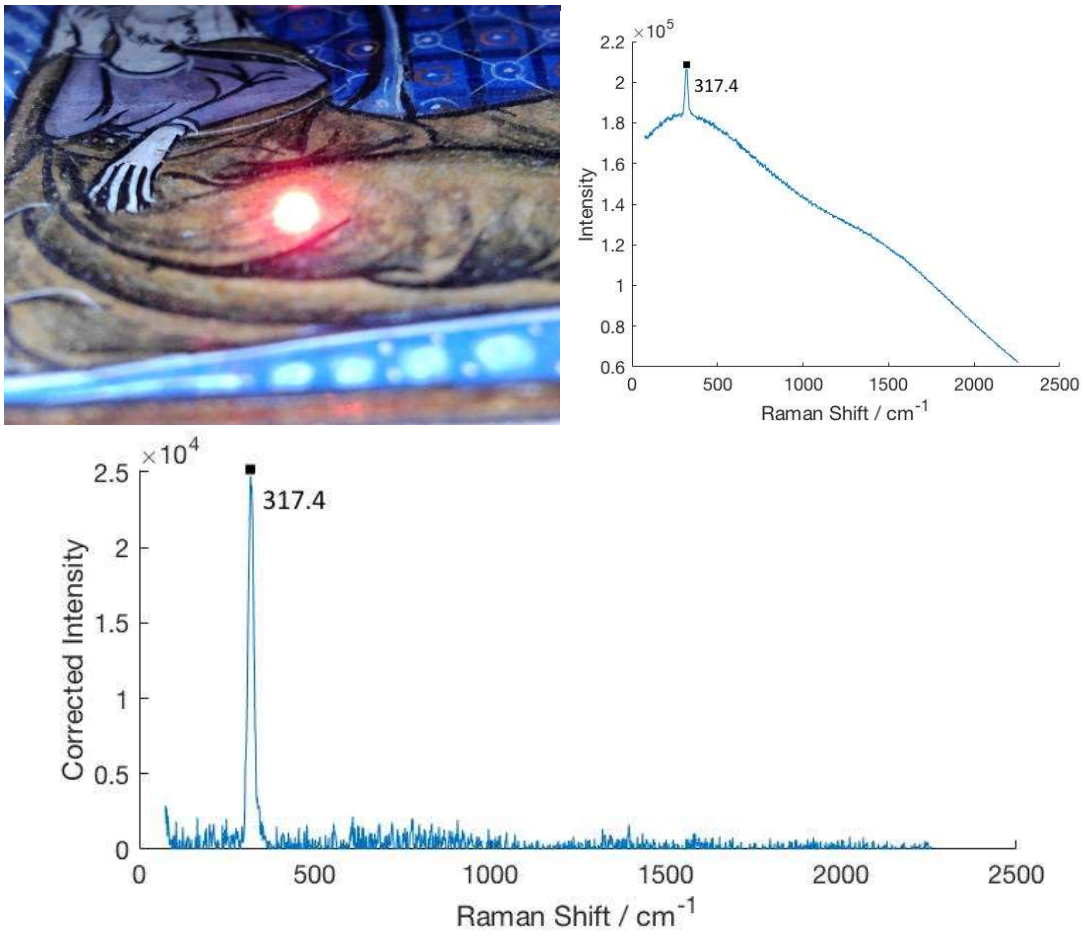


Figure 27: (top left) The area on fol. 340r that was examined, (top right) the raw Raman spectrum of mosaic gold, and (below) the corrected spectrum.

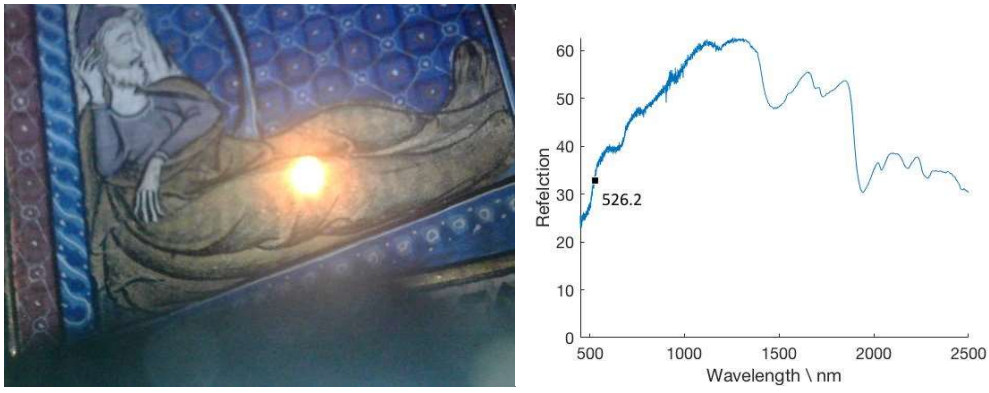


Figure 28: (left) The area of fol. 340r examined by FORS and (right) the spectrum obtained.

The FORS spectrum obtained from the mosaic gold in the manuscript is shown above in Figure 28, with the inflection point of 526 nm consistent with that given in published library data of 530 nm.[15]

Use of Blue

Both artists use the vibrant blue pigment lapis lazuli extensively and in similar ways. As discussed in chapter two, lapis lazuli was an expensive, but nevertheless ubiquitous pigment used in high-grade manuscripts of the period. In this manuscript, lapis lazuli is used for the backgrounds of many initials, over-painted with orange and black to give the impression of a wider palette of blues. The border decorations are similarly coloured. Lapis lazuli is also often used within the historiations for clothing or bedding, modulated with carbon to give the appearance of folds and shadows, as exemplified in Figure 29. It is also deployed in decorated initials, as depicted in Figure 30, where it is painted as a simple block of colour.

Figure 29: The initial on DCL A.II.3 fol. 172v (Tobit).

[15] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

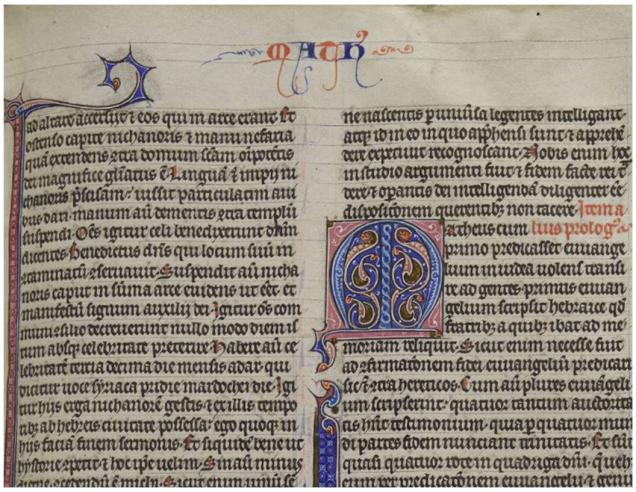


Figure 30: Fol. 340r, which shows the initial M for Matthew.

Spectra

Lapis Lazuli

As seen in Figure 31, the blue initial is coloured with lapis lazuli, the enlarged right-hand image showing where the Raman spectrum displayed in Figure 32 was obtained. The lapis lazuli peaks at 269, 552, 1097 and 1653 cm^{-1} can be seen labelled. These peaks are consistent with published library data that state that lapis lazuli has peaks at 286, 545, 1096 and 1662 cm^{-1}.[16] Further combination and overtone peaks can also be seen in the processed spectra; these have not been labelled to avoid overcrowding.

Figure 31: (left) The historiated initial on fol. 229v containing Ecclesia.

[16] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

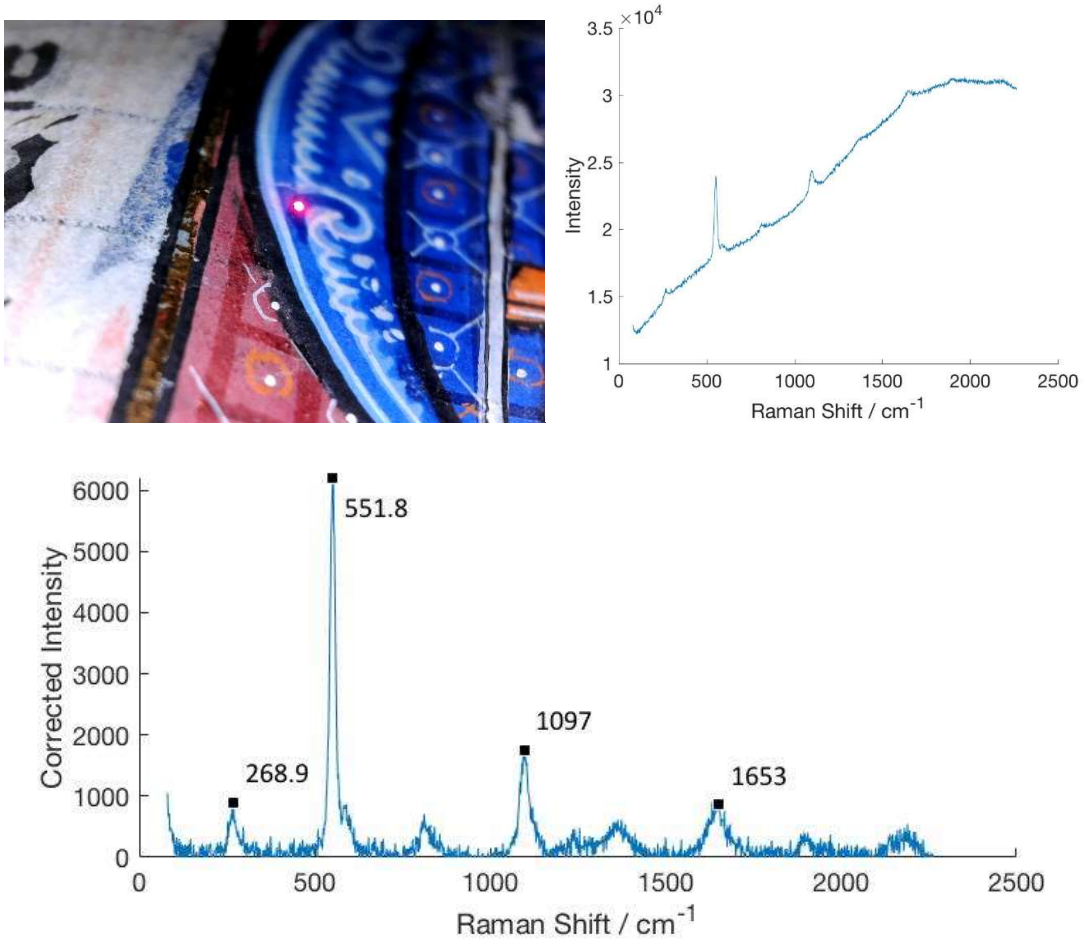


Figure 32: (top left) The spot where the Raman signal was obtained from the initial 'O', (top right) the raw spectrum obtained from the spot detailed, and (below) the spectrum after processing and background removal.

Figure 33 shows the historiated initial of Ecclesia under FORS examination. The white spot identifies the area where the FORS spectrum was obtained. The absorbance maximum at 600 nm is consistent with published data for lapis lazuli.[17]

[17] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry' p. 1491.

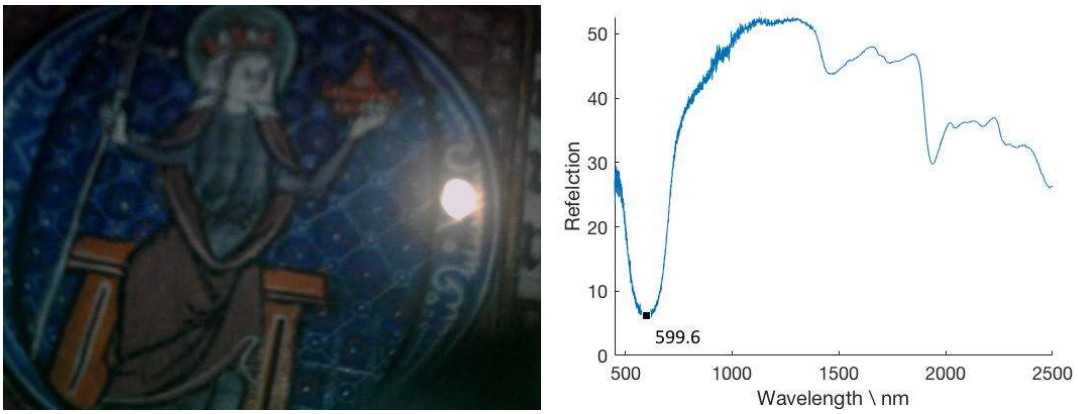


Figure 33: (left) The white spot indicates the area on the blue initial on fol. 229v where the FORS spectrum of lapis lazuli (right) was obtained.

Figure 34: (left) A photomicrograph of Ecclesia from DCL A.II.3 fol. 229v taken under white light illumination, and (right) the same under 950 nm IR illumination.

The absence of azurite in the blue paint is confirmed by the IR image in Figure 34; the blue pigment is light under IR illumination – if it were azurite, this would be dark in the NIR image. Furthermore, there are no azurite bands present in the IR portion of the FORS spectrum.

Use of Purple and Pink

Just as both artists in A.II.3 use blue for the backgrounds and border decorations, so they both also use a dusky pink colour, which, when modulated with orange and white, gives the impression of a range of pink and purple hues as shown in Figure 12. Pink is also used as a colour in its own right in the historiated scenes themselves, for example in Moses' robes, shown in Figure 35 and Figure 39.

As discussed in chapter two, pinks can be formed in a variety of ways - either by mixing a red pigment and a white one or by using a dye or combination of dyes with a substrate that together provide(s) a pink hue. It is quite possible that the pink in this manuscript has a variety of components. However,

the fact that the pink colour is so consistent throughout the book suggests that the pink was supplied to the artists in the colour that we see, and not mixed ad hoc in the workshop. More analysis of the pinks in this and the other manuscripts examined can be seen in the conclusion to this chapter.

The pink colour in this manuscript proves difficult to identify. Firstly, as seen in Figure 35 and Figure 37, the Raman spectrum shows a lot of fluorescence which swamps any small Raman peaks that might otherwise have been seen, and also suggests that the substance is organic in nature, which makes identification by this means more difficult. The lack of peaks at 251 and 342 cm^{-1} indicate that no vermilion was used.[18]

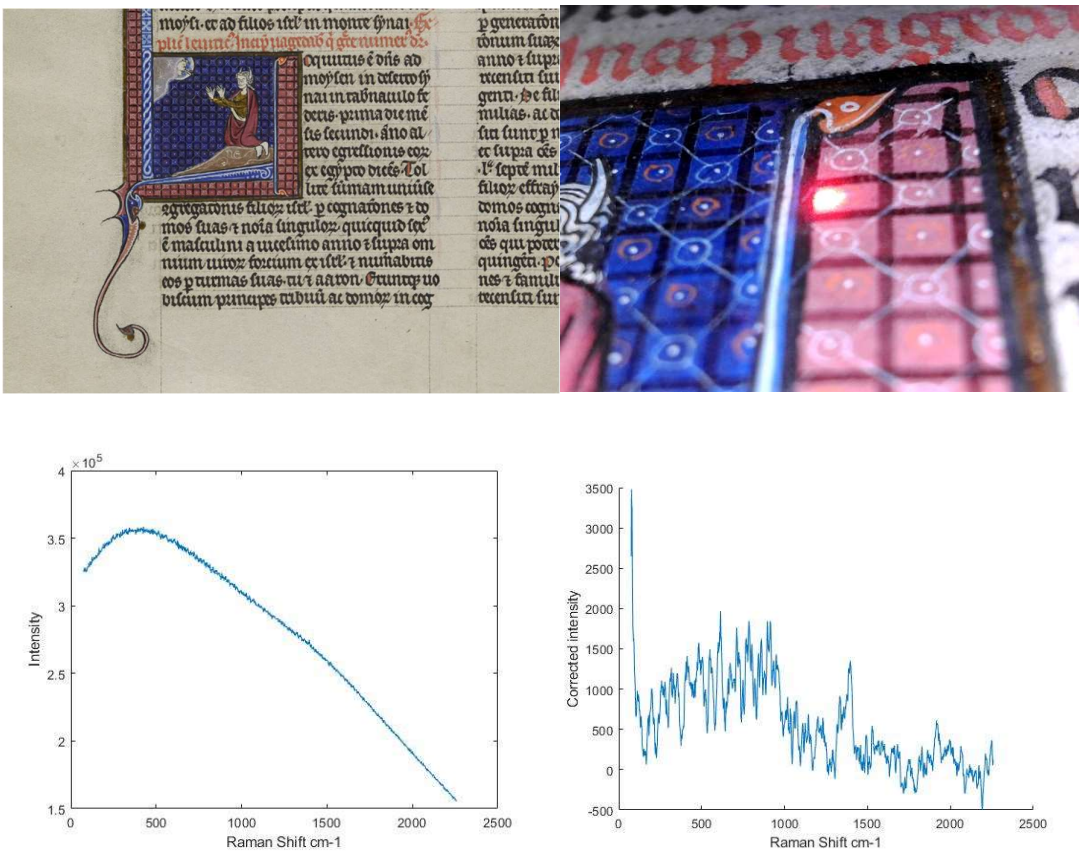


Figure 35: (top left) The historiated initial on fol. 42v with a close-up section of the initial shown on the right, indicating where the Raman signal was obtained. (Below left) The raw Raman spectrum and (right) the processed spectrum.

Figure 35 shows a typical Raman response to the pink colours throughout this manuscript, featuring fluorescence and no clear peaks, even in the processed spectra. It could possibly be argued that there

[18] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p.1222.

is a peak at around 1400 cm^{-1}, although, if so, it is not one that corresponds to any published library data for pink or red dyes or pigments.

Figure 36: The initial of the preface to Jerome on fol. 2r shown in full.

However, as seen in Figure 37, a red lead spectrum was obtained from the pink in the border of the initial on fol. 2r, depicted in Figure 36 above. This could be an erroneous result, as no other areas of the pink examined in the manuscript showed this result. A few red lead particles that were accidentally deposited on the pink surface from some sort of contamination may have been picked up by the Raman spectrometer – or it could be that the pink colour does indeed contain red lead (as part of a mixture) and that the fluorescence we saw in Figure 35 masks the red lead signal in all the other

samples taken. It may be that the red lead is part of a glaze, which again, is not detected in other pink areas.

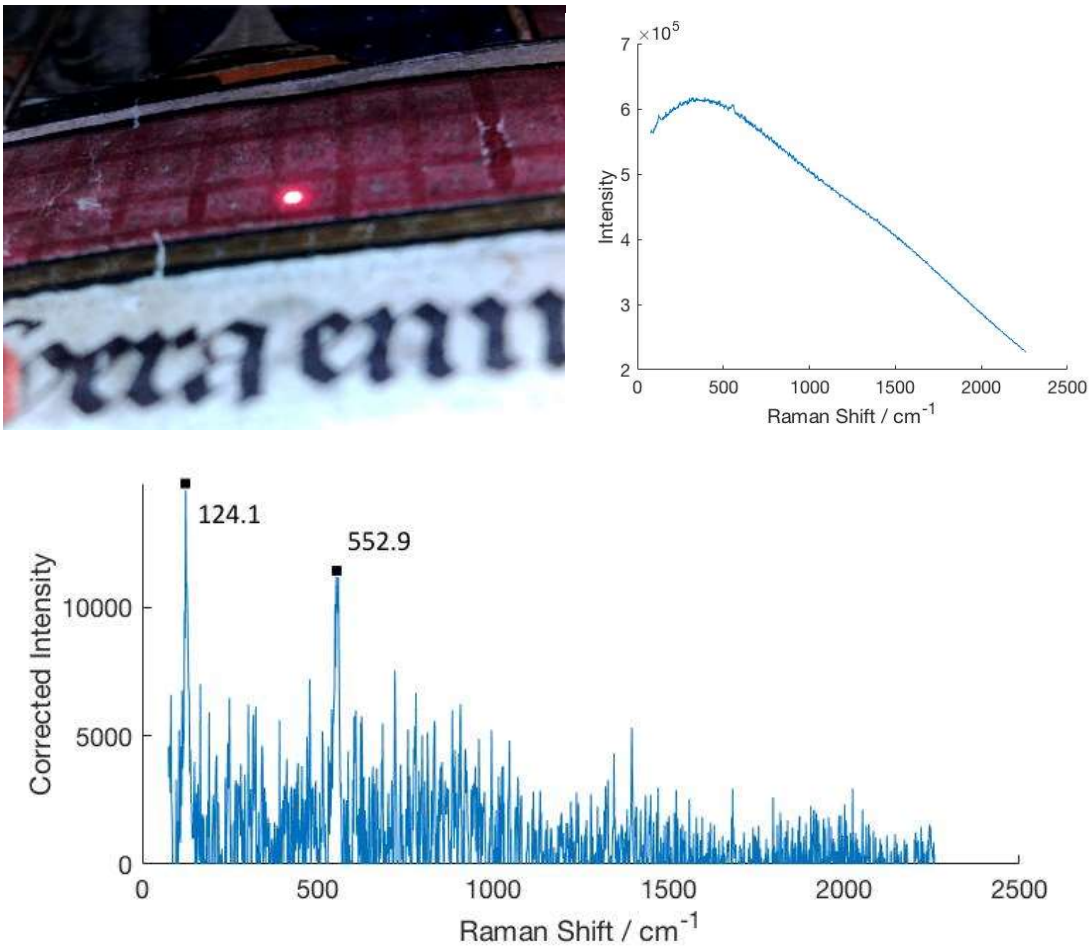


Figure 37: (top left) The area where the Raman spectrum was taken, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

The FORS spectra obtained from the pinks in the manuscript reveal further information. Firstly, the spectra for the pink used by the first artist (an example in Figure 39) and that used by the second artist (examples in Figure 38 and Figure 40) are identical, suggesting that the two artists are using the same pink colourant. Secondly, the spectra give some indication that the pink mixture could contain Brazilwood. The spectra obtained from the decoration behind the devil in fol. 2, seen in Figure 38, and the robe on fol. 42v, seen in Figure 39, and the pink in the border to the initial on fol. 240r in Figure 40, all show an absorbance maximum of between 555 nm and 560 nm.[19] The absorbance maximum

[19] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

reported for Brazilwood is 560 nm.[20] Kermes, lac and cochineal also have absorbance maxima at 555 nm, but crucially these dyes also have absorbance maximum at 520 nm, which is not displayed in these spectra.[21] Figure 38 includes an enlarged section of the spectrum, demonstrating the lack of a second absorbance point.

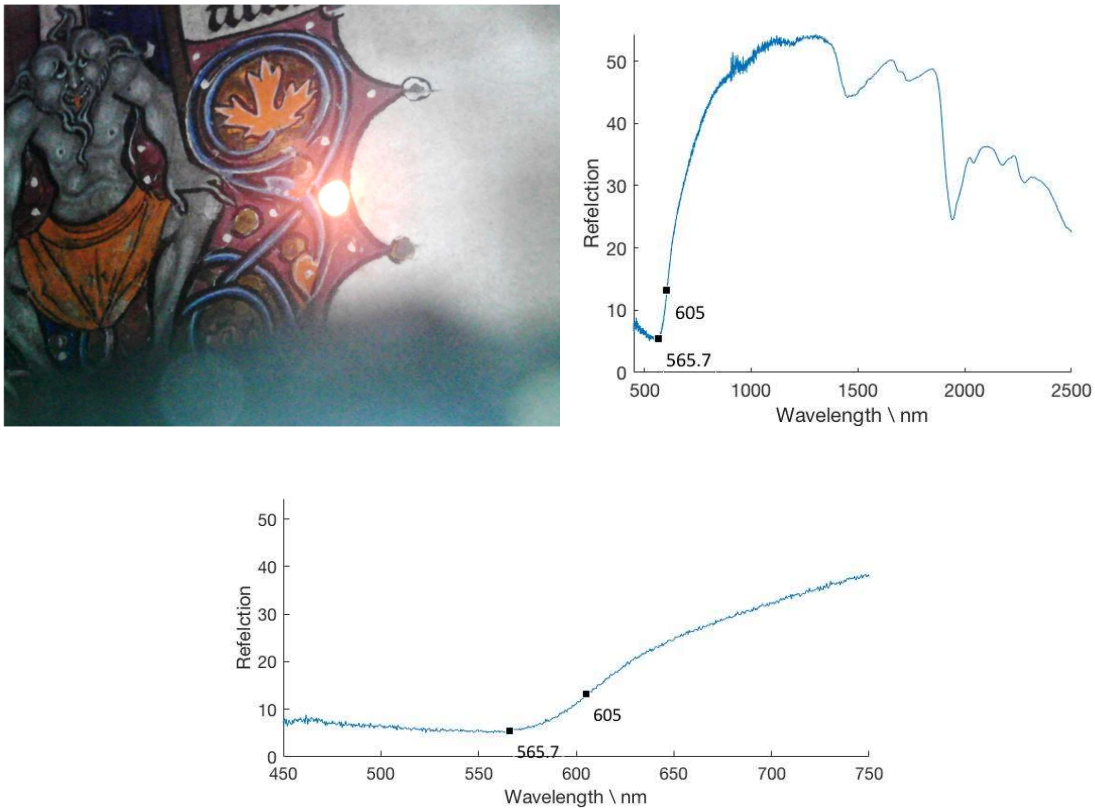


Figure 38: (top right) The pink spot on the decoration by the devil on fol. 2r where the FORS spectrum (top right) was obtained. An enlarged section of the spectrum is shown below.

[20] Aceto et al., p.1491.

[21] Aceto et al., p.1491.

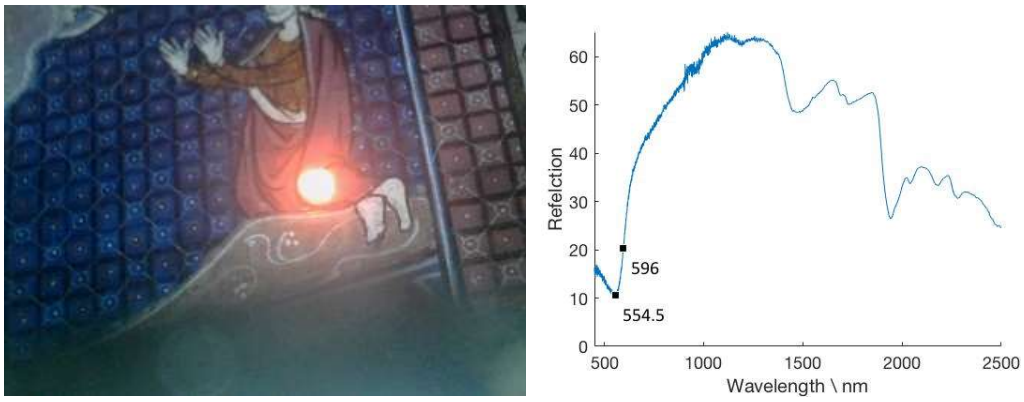


Figure 39: (left) Moses's pink robe on fol. 42v where the FORS spectrum was obtained.

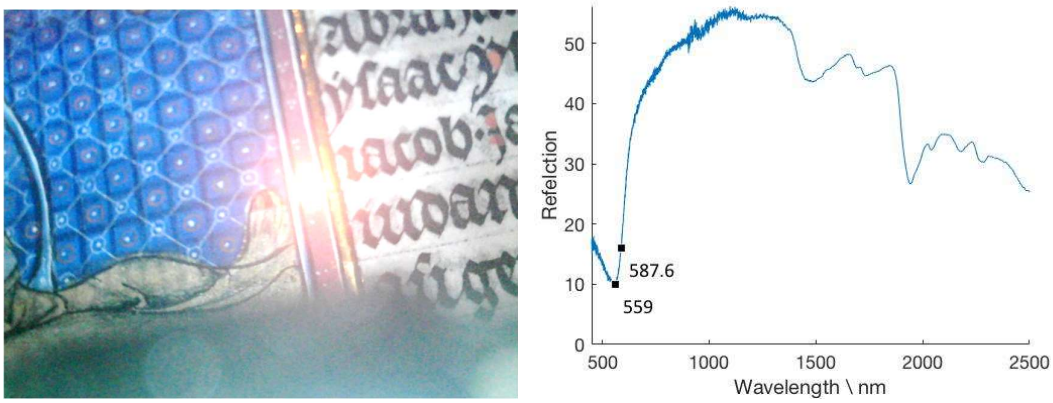


Figure 40: (left) The spot on the pink border to the historiations on fol. 340r where the FORS spectra (right) was obtained.

Figure 41: (left) A photomicrograph of a section of A.II.3 fol. 100v, and (right) the same area under side illumination.

Photomicrographs of an area containing the ubiquitous pink background show a colour that is homogenous, smooth, and matt. By contrast, the pink-red lines that articulate the background are shiny when illuminated, and are now cracked. These properties suggest that, rather than a paint, they are a glaze, where an organic dye has been mixed with a large ratio of binder (gum Arabic for example).

A paint, although usually made with a binder, would contain far less of the proteinaceous substance in relation to the pigment used, and thus when applied would not shine or crack.

Use of White

White is used extensively in this manuscript in two ways. Firstly, it is employed as a modifier to other colours, where it is seen over-painted in lines or dots, as shown in the background to the historiated initial in Figure 40, for example. Secondly, is it employed as a plain colour by itself - always for the hands, feet and faces of humans (where it is outlined in black), and occasionally elsewhere, for objects. As an example, Figure 42 shows an initial where white is deployed as the colour for skin, on the sword, and decoratively in the border of the initial.

Figure 42: The use of white in fol. 100v - Kings. The top two images show white in the face, and an object, while the lower image shows how white is used decoratively in the initial, painted over the blue and pink.

Spectra

As might be expected, white lead - a stable and common pigment that was easily obtained - was sourced for the white colour in this manuscript. White lead can be a difficult substance to obtain a

Raman spectrum from as it is not a very good Raman scatterer, and it also has no discernible features in its visible FORS spectrum although it has a narrow absorption feature in the short-wave IR region at 1447 nm characteristic of the hydroxyl band of lead white.[22]

In Figure 43, a white dot on a blue background was examined and found to be white lead, with peaks at 111, 1056 and 1386 cm^{-1}. Published data indicates that white lead has Raman peaks at 104, 1050 and 1365 cm^{-1}.

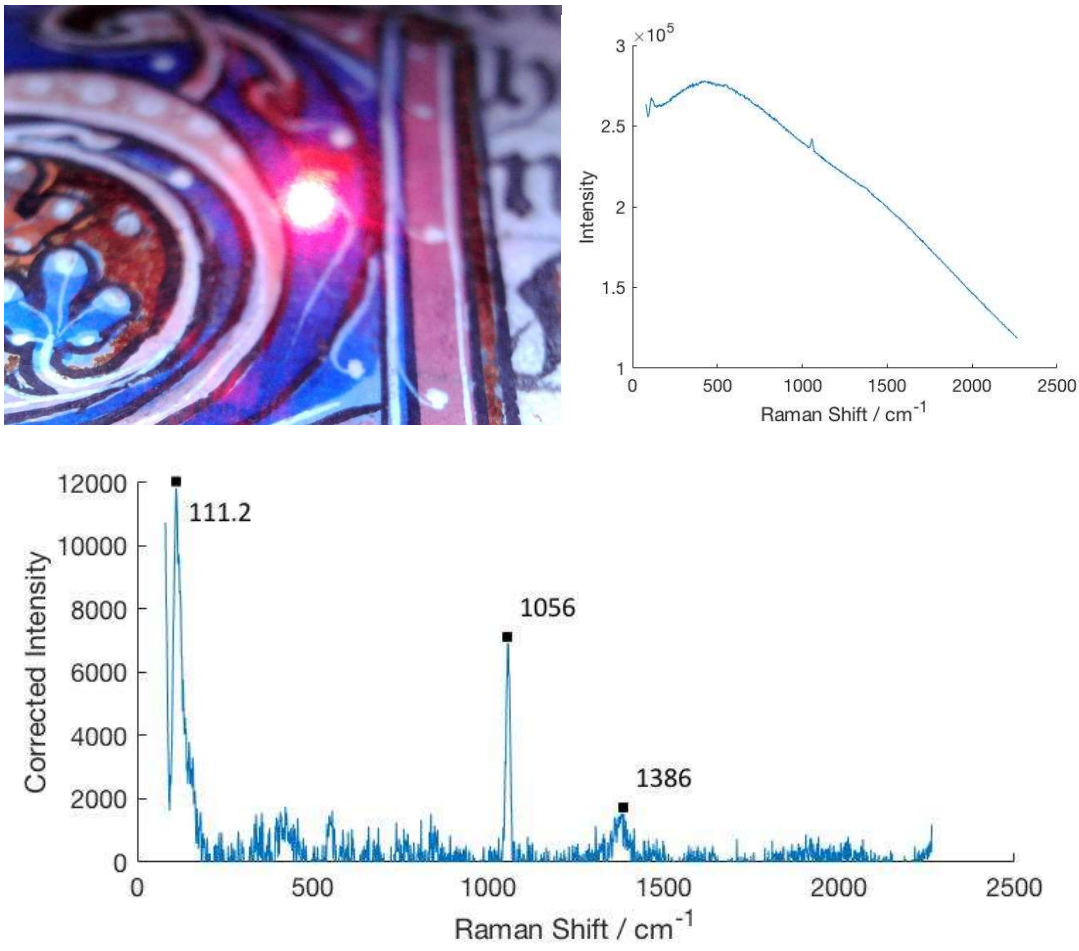


Figure 43: (top left) The spot on fol. 172v examined by Raman spectroscopy, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

[22] John K. Delaney et al., 'Visible and Infrared Imaging Spectroscopy of Paintings and Improved Reflectography', *Heritage Science* 4, no. 1 (16 March 2016), p. 97.

Use of Orange

As previously discussed, orange is employed on top of other pigments such as white lead and lapis lazuli, to modify their colours to provide a textured background and to give the impression of a wider palette. When deployed as a colour on its own, it is applied as a plain block of bright colour. Black and/or white may be added on top to provide form or perhaps detailing, but these colours are never used to change the tone of the orange itself. This is typified in the orange seen in Figure 44, where it is seen in a block of colour for the bench and is employed for the object in Ecclesia's hand. The orange is likely to have been used in its unadulterated form, not mixed with another colourant. Black and white (likely white lead and carbon) provide outlines and form to the orange shapes.

Figure 44: A.II.3 fol. 229v Song of Songs – Ecclesia's bench and object.

Spectra

The orange pigment employed in this manuscript is identified as red lead. In Figure 45, the FORS spectrum of Ecclesia's bench, depicted in Figure 44, displays the characteristic inflection point of red lead at about 568 nm. This is consistent with published sources that state that the inflection point is at 565 nm.[23]

[23] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

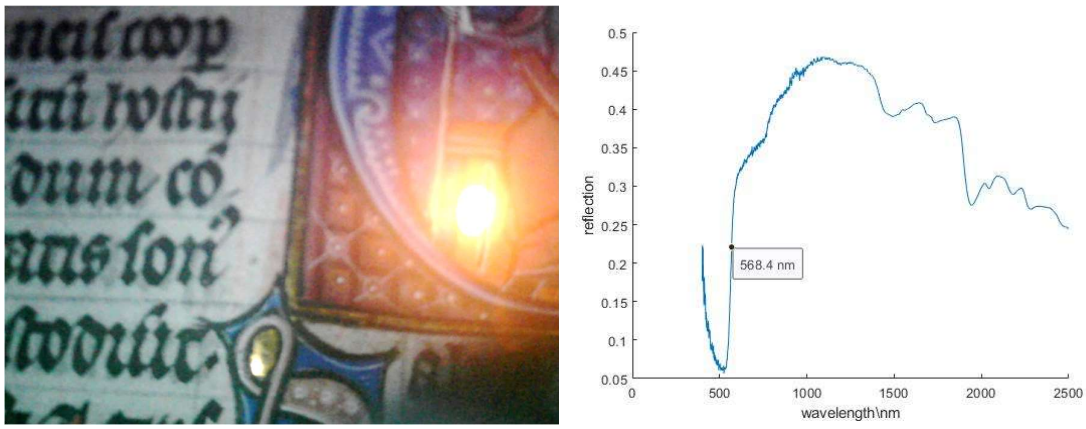


Figure 45: (left) On fol. 229v the spot on the orange bench where the spectrum of red lead (right) was obtained.

In Figure 46, the spot in the picture on the left indicates whence the Raman spectrum shown was taken. The peaks at 128 and 556 cm^{-1} are indicative of red lead, consistent with published data that have red lead peaks at 121 and 549 cm^{-1}. The peak seen at 397 cm^{-1}, along with the smaller peaks between 128 and 554 cms^{-1} (unlabelled for clarity) are also consistent with red lead.

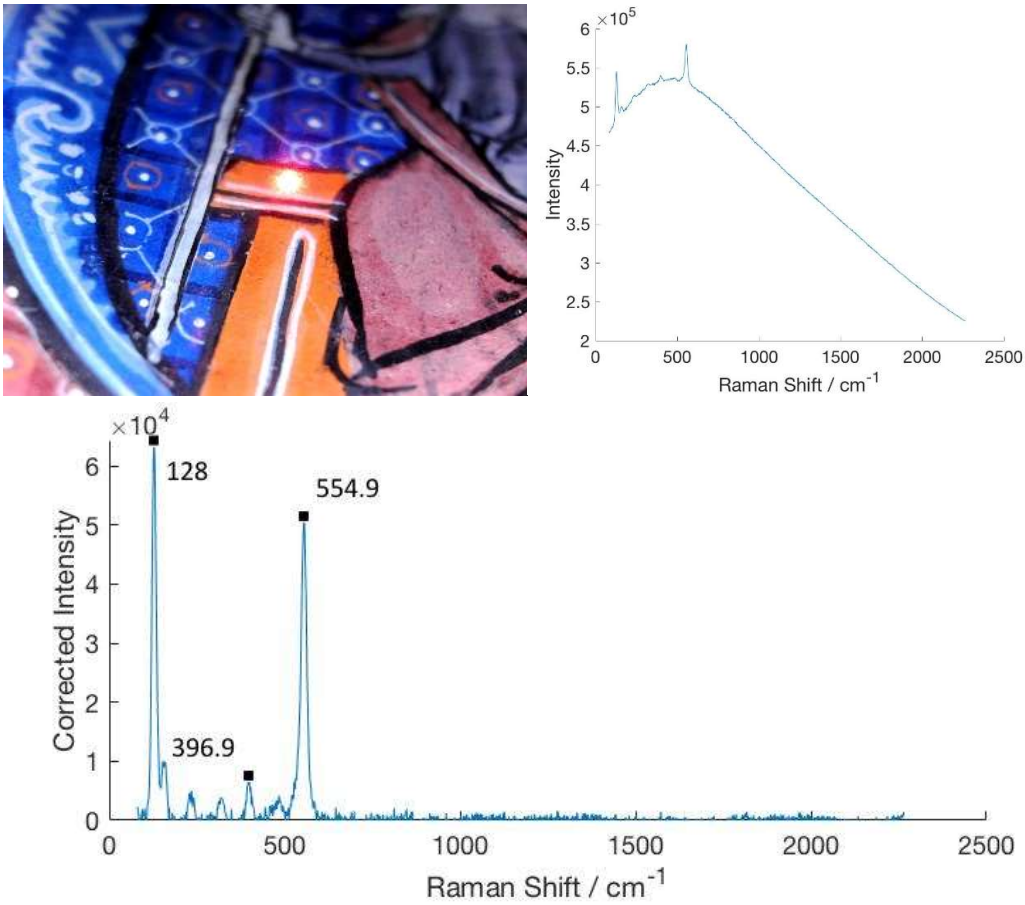


Figure 46: (top left) The spot on the orange bench on fol. 229v reveals the raw Raman red lead spectrum (top right) and the processed (bottom).

Another usage of red lead, seen often throughout the manuscript, is for orange leaf motifs - plain blocks of colour with only white detailing on top. An example of one from fol. 76v is shown below in Figure 47, alongside its Raman spectrum, which is again consistent with published data for red lead.

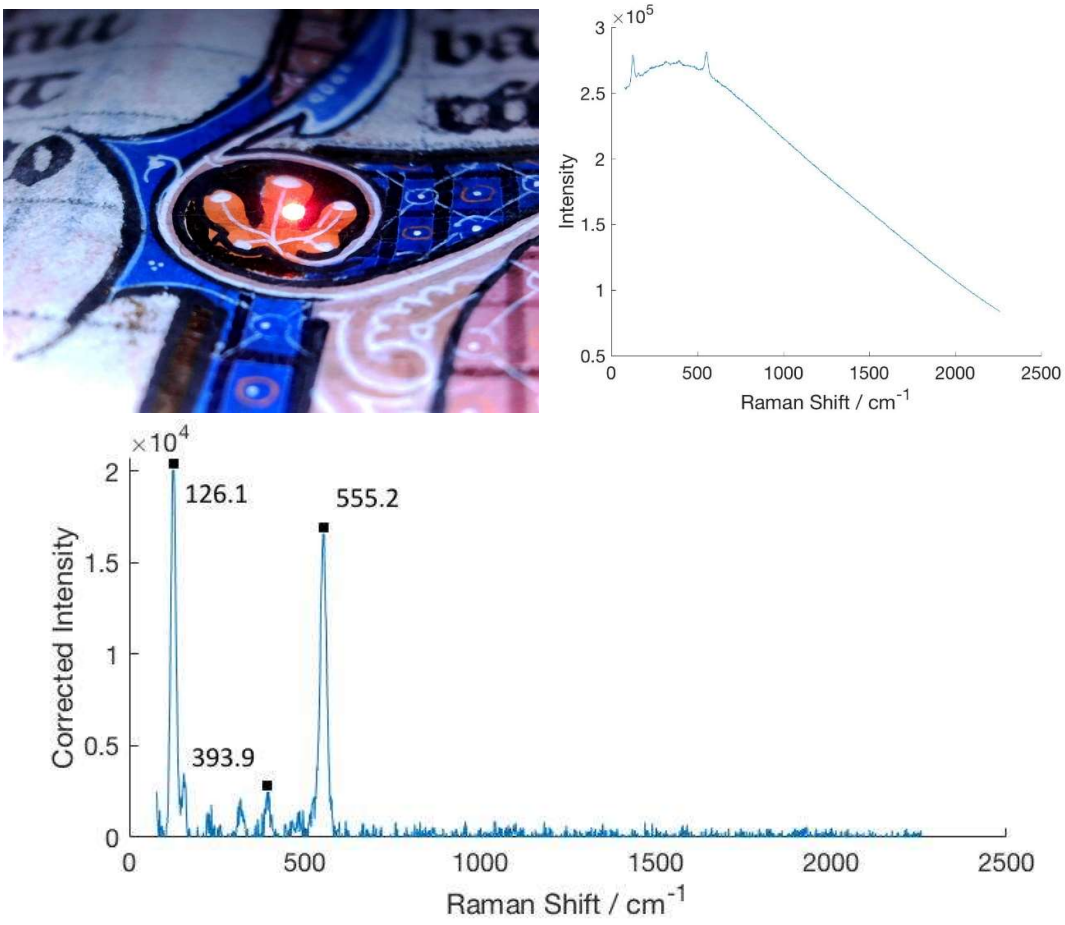


Figure 47: top (left) A red lead orange leaf motif on fol. 76v that was examined, (top right) the raw spectrum obtained, and (below) the processed spectrum.

Use of Green

The colour green, either on its own or as an addition to another colour, is not seen at all in the manuscript until fol. 225v, where it features prominently in the knight's robe and in the leaf motif as seen in Figure 48. From then on in the manuscript it is used for Ecclesia's halo on fol. 229v and in several other historiated initials for clothes and blocks of colour, and very occasionally as a leaf motif.

Figure 48: The first use of green seen in A.II.3 appears on fol. 225v, shown here.

Much like the use of red lead, the green is deployed as a 'pure' colour and modulated only by black or white and even then, only to provide form or details on top, not to change the tone of the colour. The leaf motif has the same shape and plain appearance as that described in relation to the use of orange, and, like that case, it too is highlighted with white.

Spectra

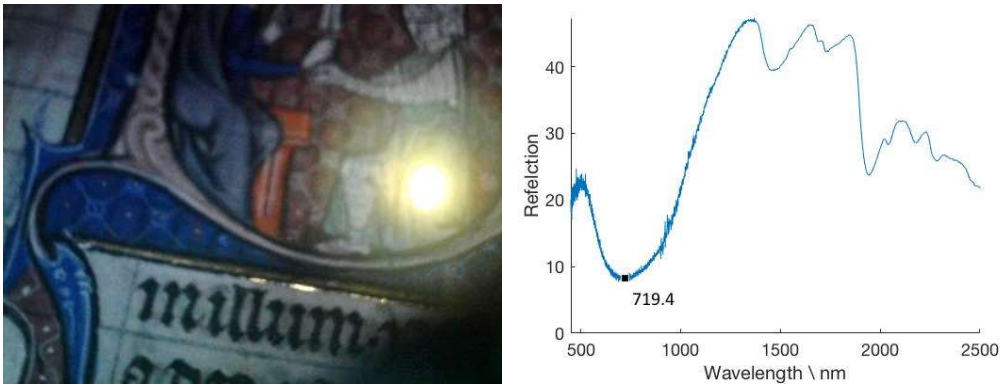


Figure 49: The spot on the knight's robe on fol. 225v (left) where the FORS spectrum (right) was taken

As seen in Figure 49, the FORS spectrum of the green has an absorbance maximum of 719 nm. This is consistent with published data for FORS spectra that states that verdigris has an absorbance maximum of 720 nm.[24]

[24] Aceto et al., p. 1491.

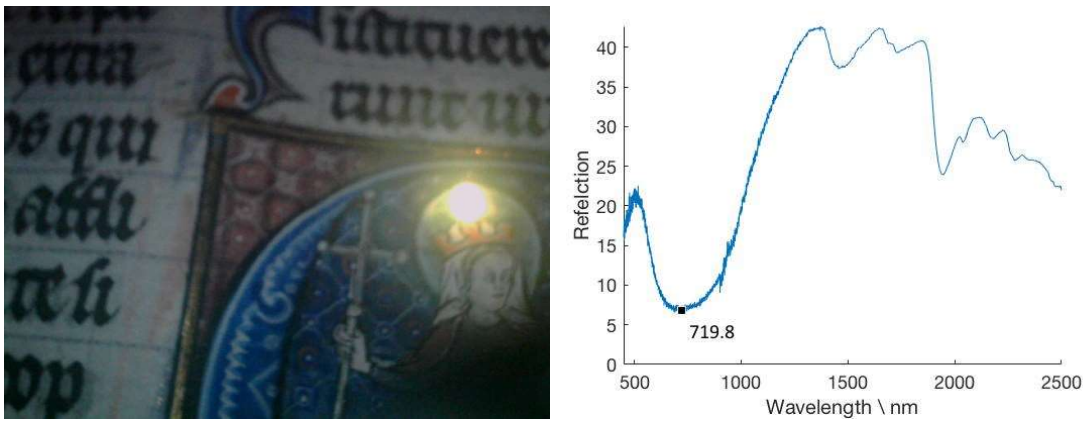


Figure 50: (left) The spot on the green halo on fol. 229v where the spectrum of verdigris (right) was obtained.

Similarly, Ecclesia's green halo, on fol. 229v, provides a spectrum with an absorbance maximum of 720 nm, consistent with the published data for verdigris.[25]

Copper green or verdigris would not be expected to show a Raman signal at 633 nm. This is because green absorbs the red laser light and also the scattered Raman signal. An attempt at recording a Raman spectrum was made from the point shown by the laser in Figure 51, on the green leaf. As can be seen from the resulting unprocessed and processed spectra, the spectrum returned does not show any peaks and shows very low fluorescence. The intensity of the laser light returning to the spectrometer, which is usually of the order 10^4 counts per second, can be seen to be very low in comparison.

[25] Aceto et al., p. 1491.

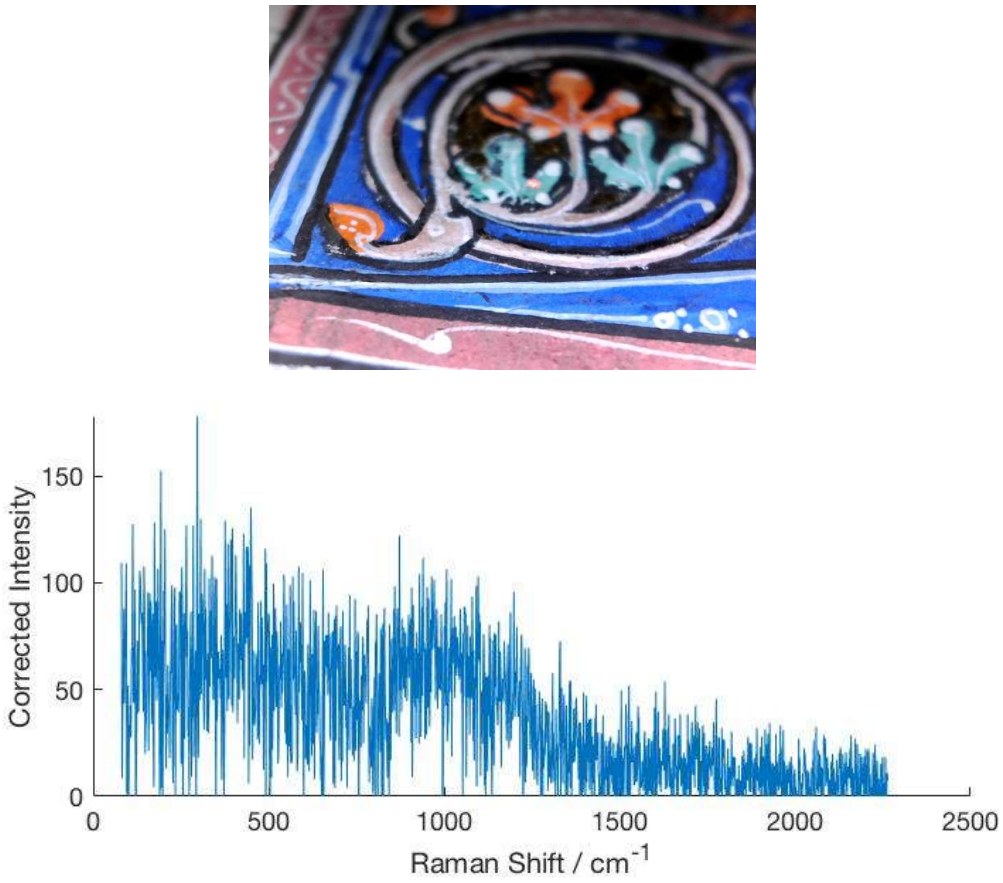


Figure 51: (top left) Fol. 225v where the Raman spectrum was taken, and (bottom) the processed spectrum.

As shown above and repeated in Figure 52 below for ease, the green pigment is seen to be dark in the NIR suggesting that the pigment is copper-based. The patchy nature of the application of the pigment seen under the IR illumination (an effect exacerbated by subsequent losses) corresponds with darker and lighter areas under white-light. This could simply be areas with more and less paint applied or could be that the darker areas are mixed with carbon, which appears dark under IR illumination, although the latter is unlikely.

Figure 52: (left) A photomicrograph of Ecclesia from DCL A.II.3 fol. 229v taken under white light illumination, and (right) the same under 950 nm IR illumination.

Use of black

Black is used extensively throughout the manuscript to outline drawings or to provide detail and form to other colours. In Figure 53, black can be seen outlining all the figures and shapes, as well as defining the folds of the clothes and outlining the facial features. It is also seen in blocks of colour, in the same Figure, for example, where black is employed for the leg of the two right-hand figures and for the king's feet.

Figure 53: DCL A.II.3 fol. 100v (Kings).

Spectra

The black pigment used both for outlining and for blocks of colour is carbon. Carbon can be easily distinguished in two ways. Firstly, it strongly absorbs visible and infrared light and so its FORS spectrum, as can be seen in Figure 54, gives a spectrum with a very flat profile showing very little reflectance.

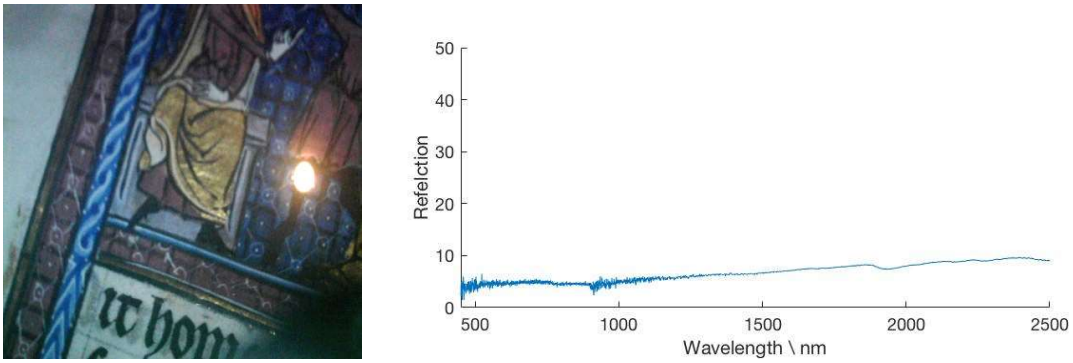


Figure 54: (left) The spot on the black leg on fol. 100 v) where the FORS spectrum (right) was obtained.

Secondly, carbon has an identifiable Raman spectrum with broad peaks at 1335 and 1602 cms^{-1}, which sit on a broad background of fluorescence in the unprocessed spectrum.[26] Again, these are different peaks to those mentioned earlier, as the peaks can change depending on the crystallinity of the sample, and thus appear within a range. An example of carbon spectra can be seen in Figure 55.

[26] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

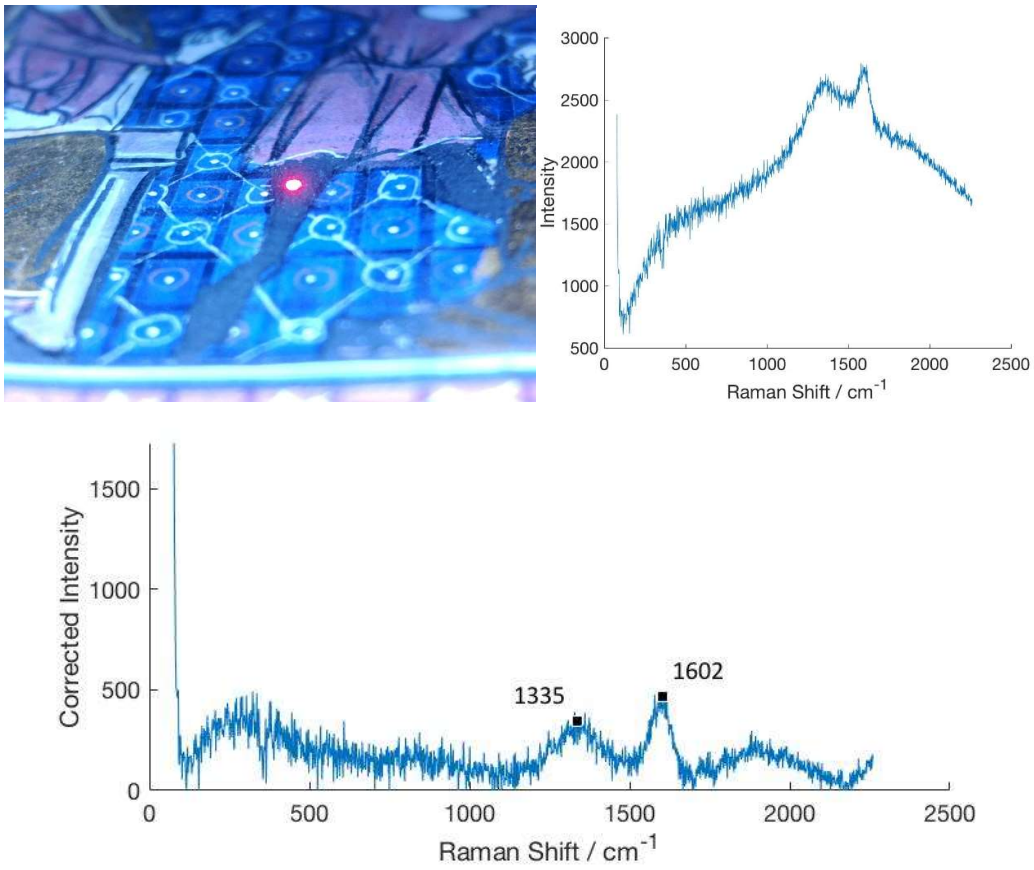


Figure 55: (left) The spot where the Raman spectrum was taken. The middle picture shows the unprocessed spectrum and the right picture the processed spectrum.

In addition to carbon black, indigo is used, infrequently, to provide a dark line to add detail to an image. Figure 56 shows that the dark outlining of the folds of clothing is indigo, from the peaks at 256, 550, 606, 1255 and 1587 cm^{-1}.[27]

[27] Marucci et al., p. 1222.

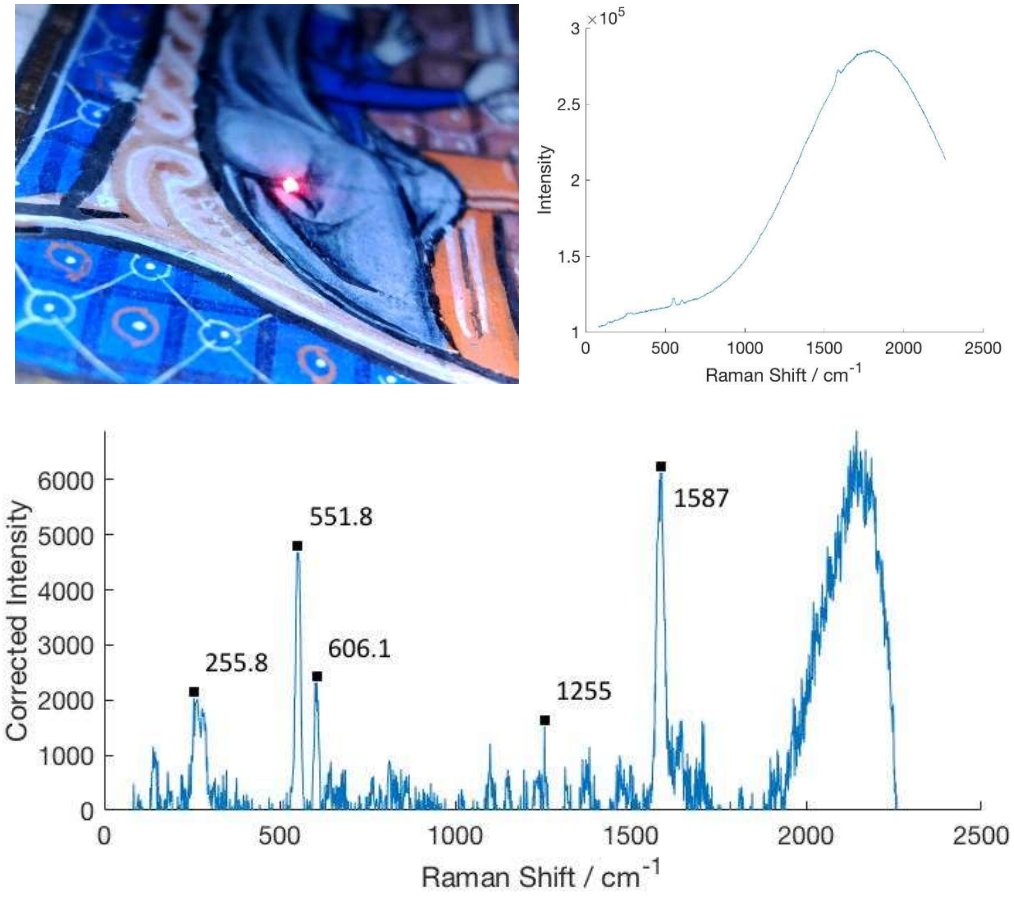


Figure 56: The spot on fol. 172v where the Raman spectrum was taken, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

Use of brown

Figure 57: (left) The historiated initial on fol. 42v shows the brown ground, and (right) the initial on fol. 299v shows the brown mound and brown lions.

Brown is not a colour that features prominently in the palette of A.II.3, employed only, it seems, when the subject matter rendered its deployment unavoidable. In Figure 57, the brown ground underneath the figure of Moses is shown on the left, and the brown cave and brown lions are shown under Daniel, on the right. In both these pictures, it would seem that the brown colour is obtained by using a mixture of pigments as indicated by the inhomogeneous nature of both colours. The browns in the pictures seem, to the eye, to be different one from the other, with the brown in Daniel's cave being more black-brown than the lighter brown of the ground under Moses.

Spectra

Figure 58 shows the spot on the brown ground underneath Moses on fol. 42v, which yields the processed Raman spectrum also shown. This spectrum provides no clue as to the makeup of the brown pigment(s), as there are no discernible peaks.

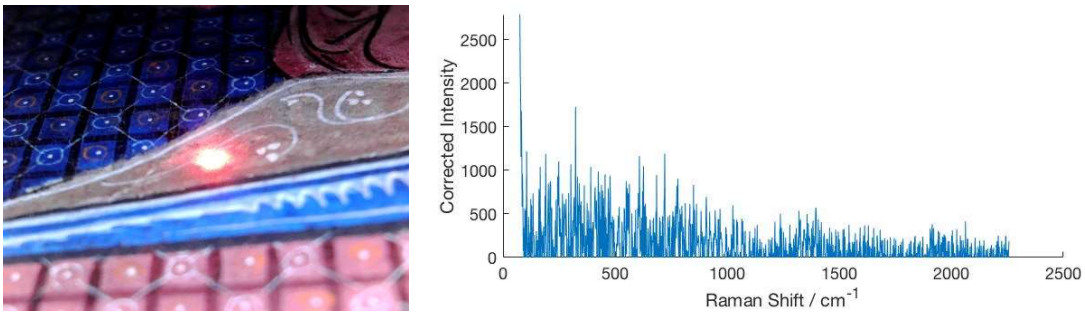


Figure 58: (left) the spot on fol. 42v where the Raman spectrum was taken, and (right) the processed spectrum.

The FORS spectra, shown in Figure 59, similarly provides no real information as to the pigments used. The absorbance maximum of approximately 510 nm does not correspond with any published data for brown pigments yet seen.

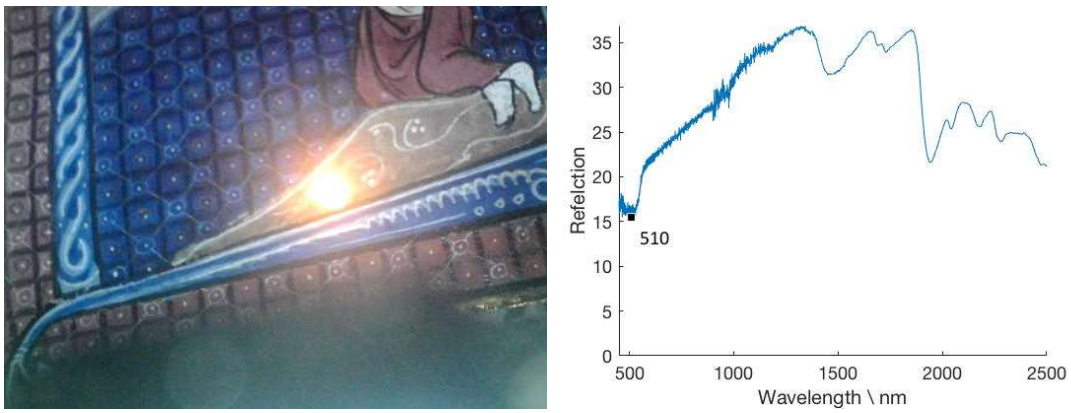


Figure 59: (left) The spot on fol. 42v where the FORS spectrum (right) was obtained.

However, the brown used on fol. 299r does yield some evidence of its constituents, as the Raman spectrum reveals some pigments in use. The peaks at 264, 549 $cm^{-}$and 1583 cm^{-1}, are consistent with those for indigo. There is also a broad band of fluorescence centred at about 2135 cm^{-1} which is typical of indigo. The peak at 143 cm^{-1} may be massicot or anatase. It seems that the brown here is a mixture of several colours, including indigo.

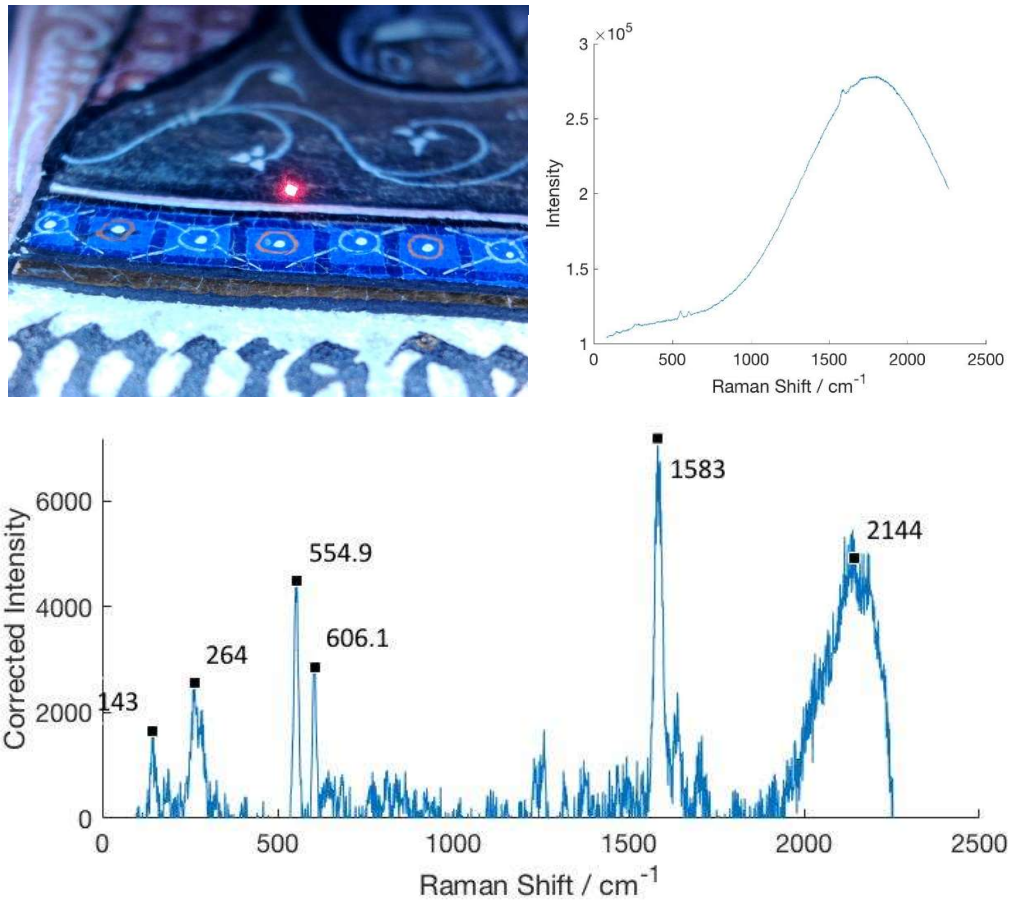


Figure 60: (top left) The spot on fol. 299r where the raw Raman spectrum (top right) and the processed spectrum (bottom) was obtained.

The FORS spectrum of the same brown colour, as seen in Figure 61, displays an inflection point and possibly two absorbance maxima, although these do not correspond to anything in published works. This is not unexpected - a mixture of pigments, which it is more than likely this brown is, is difficult to identify with FORS because, as described in chapter 4, the features of the spectrum change with the addition of each colourant, particularly in the visible.

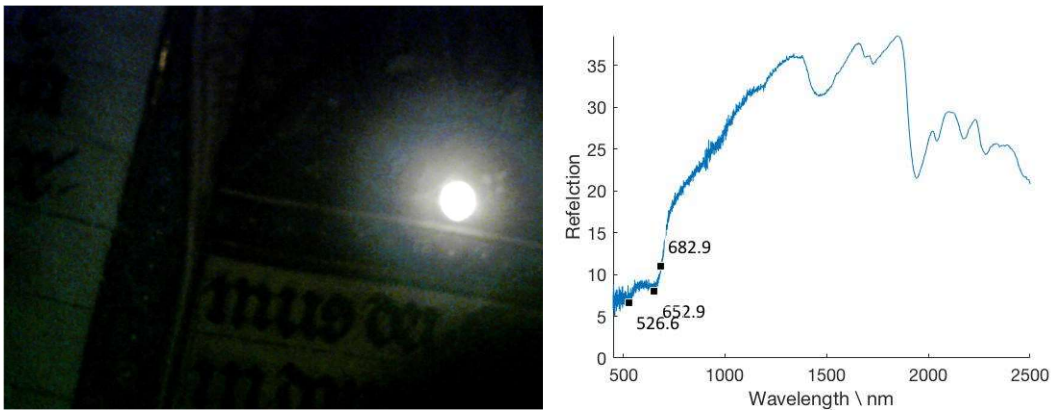


Figure 61: (left) The spot on the brown of fol. 229r where the FORS spectrum (right) was obtained.

Use of Yellow

As shown below in Figure 62, there are some extremely small areas of a creamy yellow deployed for hair and occasionally for contouring as seen in the faces in Figure 4 . These areas are too small to analyse by FORS, but are likely to be organic – possibly saffron or weld – as they do not display the strong colour, or Raman spectrum, associated with orpiment.

Figure 62: (left) A photomicrograph of DCL A.II.3 fol. 100v, and (right) under UV illumination.

Text and text ornamentation

Rubrication was a highly formulaic way of decorating that required less skill than painting artwork. Accordingly, it would generally not be undertaken by illuminators but rather by scribes or specialised rubricators. In A.II.3 this ornamentation takes the form of text initials, waterfalls that cascade down the side of columns with text initials, running headings, traditional red rubrics for chapter headings, red strokes on capital letters, and flourishing around corrections in the margins.

Red and blue are the most common colours used for text ornamentations (indeed the term 'rubrication', like 'rubric' is derived from the Latin 'ruber', the adjective for red). A.II.3 is no exception, and red and blue are the only colours used for text decorations.

Black Ink

It would normally be expected that a manuscript such as A.II.3 would be written in oak gall ink, the making of which is discussed in chapter two. Oak gall ink can be identified by its reflectance spectrum. However, it appears that the ink in A.II.3 is oak gall with the addition of carbon. Black text from fols. 3v, 21v, 74v, 123v, 193v, 330v and 394v, along with a marginal correction on 394v were all examined with Raman and found to contain carbon, with the exception of 74v, which did not. Unsurprisingly, the addition of carbon to oak gall ink would have made it darker, and the ink in A.II.3 does appear very black to the eye.

Spectra

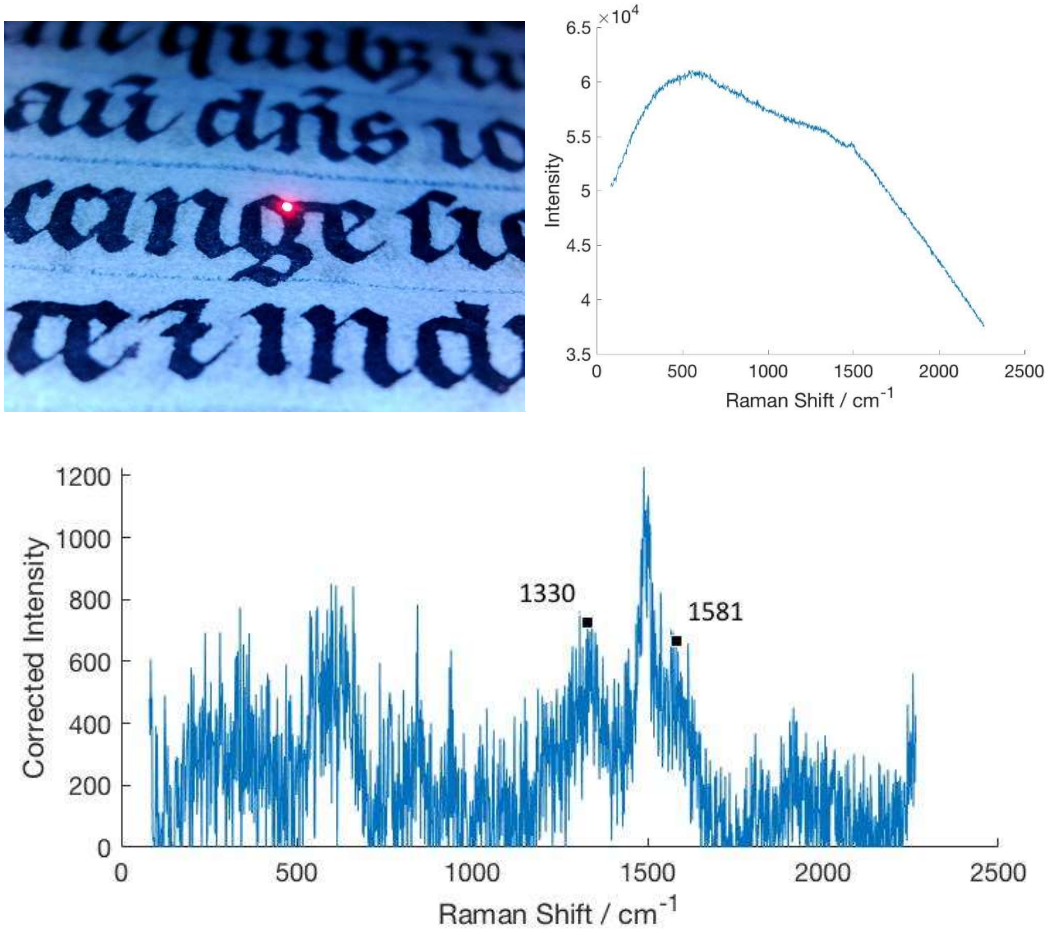


Figure 63: (top left) The black ink of fol. 193v that was examined, (top right) the raw Raman spectrum obtained and, (bottom) the processed spectrum.

As can be seen in Figure 63, the Raman spectra reveals a pigment with peaks at 1333, 1490 and 1581 cm^{-1}. This is oak gall ink. [28]

Waterfalls

The red and blue waterfalls that accompany decorated initials (seen in full in Figure 2) are also vermilion and lapis lazuli, as shown in Figure 64 and Figure 65.

[28] Marucci et al.

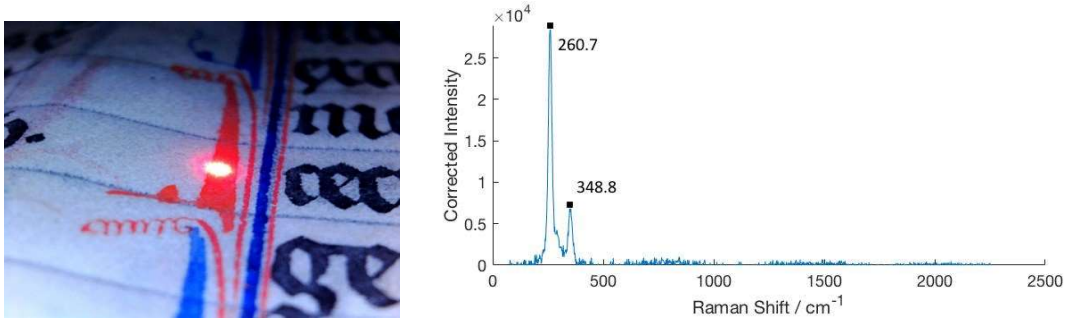


Figure 64: (left) A red waterfall on fol. 100v, and (right) the processed Raman spectrum showing vermilion.

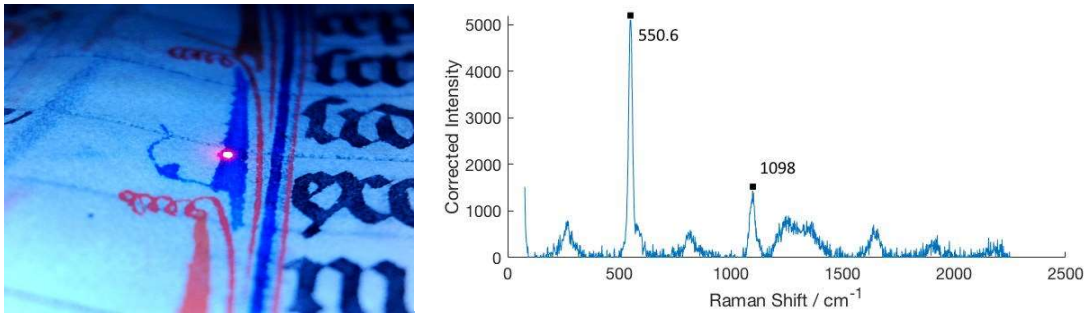


Figure 65: (right) a blue waterfall on fol. 100v, and (right) the processed Raman spectrum showing lapis lazuli.

Rubric

As seen in Figure 66, rubrication from fol. 76v is vermilion, as confirmed by published data.[29]

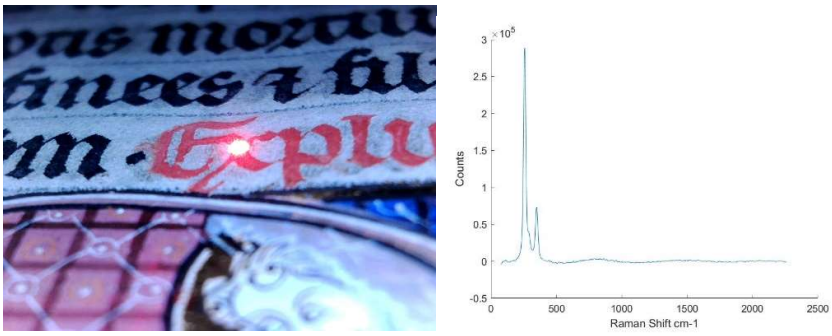
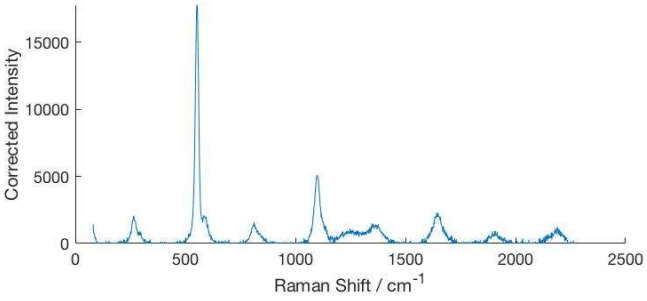


Figure 66: (left) The spot on the rubrication on fol. 76v and (right) the processed Raman spectrum.

[29] Marucci et al., p. 1222.

Index

As can be seen in Figure 67, the red and blue initial text ornamentations are vermilion and lapis lazuli, as expected.



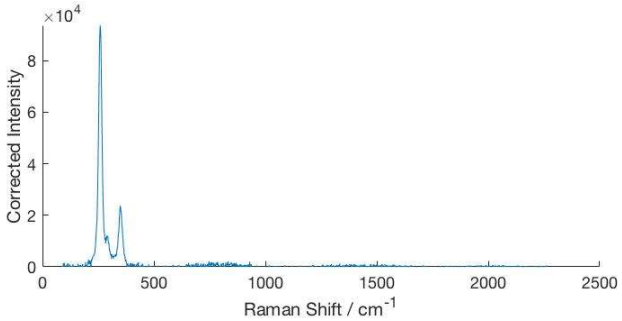


Figure 67: (top) Image of the index on fol. 438r, (middle left) the blue text ornamentation examined and its accompanying processed Raman spectrum, and (bottom) the red text ornamentation examined and the accompanying Raman spectrum.

The Flourishing of the Corrections

Whilst the blues in the other text ornamentations are lapis lazuli, the corrections at the side of the main text are azurite, as seen in Figure 68. Here the FORS spectrum shows azurite, with two narrow

absorbance bands at 2281 and 2350 nm, consistent with published data which has the bands at 2284 and 2351 nm.[30]

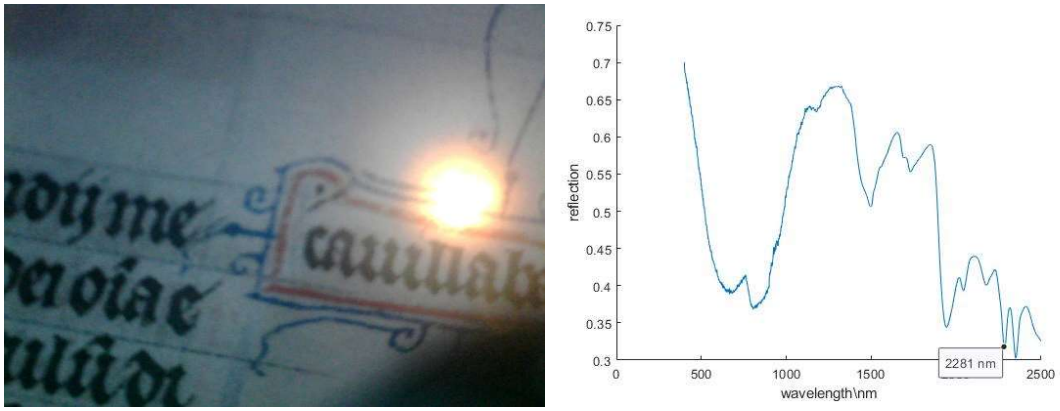


Figure 68: (right) The FORS spectrum of the blue flourishing around a correction (fol. unknown).

Further Comments on the Palette as a Whole

The range of pigments used in A.II.3 – carbon, copper green, white lead, mosaic gold, gold leaf, red lead, vermilion, lapis lazuli, lapis ash, azurite, and indigo, plus other organic lakes and glazes whose composition is at present unascertained – are able to create a palette which is more than the sum of its parts, and give the impression of a much broader range of pigments than is actually used. This is in part achieved by clever moderation by orange, white and/or black.

Most of the pigments used are not particularly surprising, as they are typical pigments for the thirteenth century. However, the presence of mosaic gold is notable; one early use reported in previous literature dates from the fourteenth century.[31]

[30] John K. Delaney et al., 'Use of Imaging Spectroscopy, Fiber Optic Reflectance Spectroscopy, and X-Ray Fluorescence to Map and Identify Pigments in Illuminated Manuscripts', *Studies in Conservation* 59, no. 2 (March 2014), p. 97.

[31] Nicholas Eastaugh, ed., *The Pigment Compendium: A Dictionary of Historical Pigments* (Amsterdam; Boston: Elsevier Butterworth-Heinemann, 2004), p. 274.

Durham University Library Cosin V.v.17

Description and Provenance

Cosin V.v.17 is a pocket-sized Paris Bible with 320 leaves, measuring 127 mm by 92 mm; its diminutive size can be appreciated from Figure 74. Made in either Southern France or Northern Italy in the thirteenth century, it is an example of a 'Paris Bible' but is not one that was made in Paris. At one point in its history, this book belonged to James IV Scotland (d. 1513), as there is an inscription on one of the inner fly-leaves, fol. 2r, which describes how the king left the book to the Ogilvy family. The inscription is shown in Figure 69.[32] The book is a Latin Vulgate Bible supplemented by an (incomplete) list of Hebrew names with their meanings.

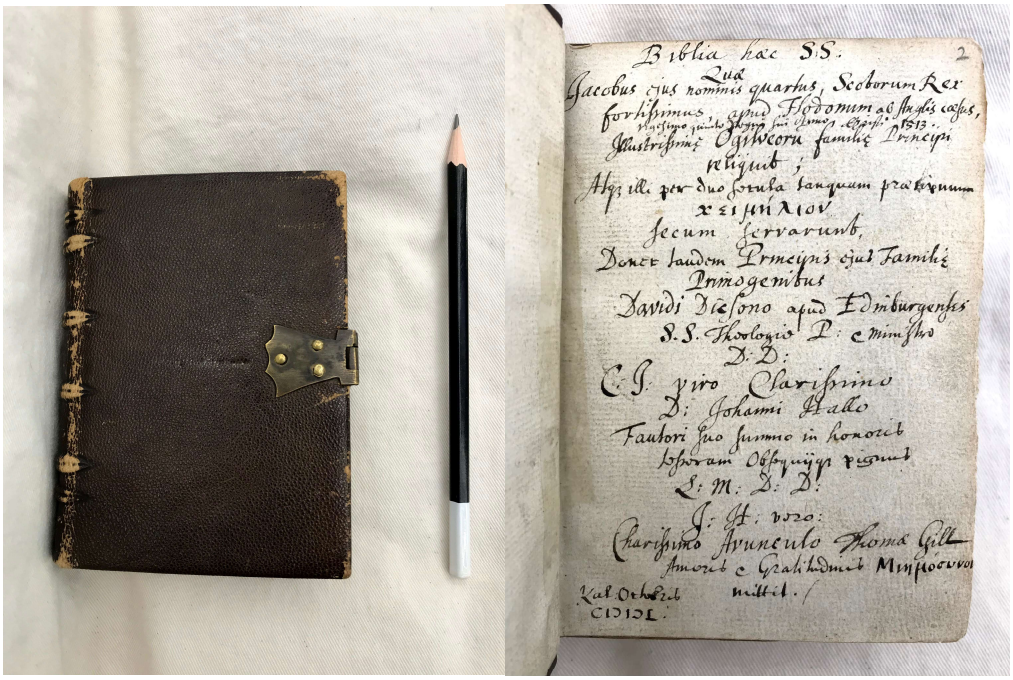


Figure 69: Cosin V.v.17 with a pencil for scale. The binding is a 19th-century one.

Codicology

Quire Formation

Most of the twenty-eight quires from which the volume is composed are 12s; however, two 8s, two 14s, and one 6 are also used. Respectively these are quires II and IV; X and XXVIII; and VI.

[32] Richard Gameson, ed., *Treasures of Durham University Library* (Durham-London, 2007), p. 52.

Parchment and Ruling

The parchment is very thin when compared to that of DCL A.II.3, for example, and is extremely uniform in thickness as all the leaves measured were 0.08 mm thick. The thinness of the parchment is crucial to accommodating 320 folios in a pocket-sized volume. The parchment is of fair quality, although there are many pages that show hair follicles. These are arranged within the quires, so that hair side faces hair side, and flesh faces flesh. The parchment was non-invasively peptide fingerprinted by a team at York University and found to be derived from goat skin.[33]

There are no visible prickings, having been lost through trimming. The ruling is done in lead, as can be seen most clearly in Figure 70. There are 50 lines on each folio, with the exception of one quire, quire V, which has 51 lines.

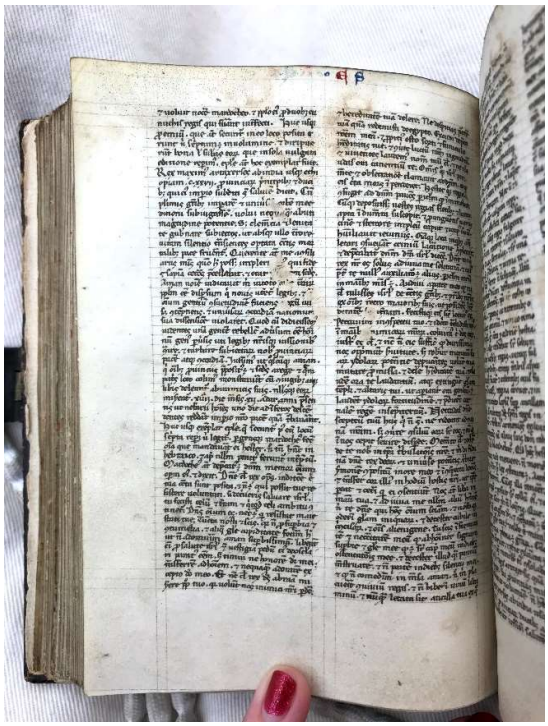


Figure 70: Fol. 131v, clearly showing the ruling pattern and some patches of ink loss.

Despoliation

The top edge of the book is black, which, considering the other two fore-edges are painted gold is most probably a result of soot damage.

[33] For the process see: Fiddyment et al., 'Animal Origin of 13th-Century Uterine Vellum Revealed Using Noninvasive Peptide Fingerprinting'.

There is major damage to the first few pages of the book, as can be seen in Figure 72, probably caused by either damp, or by use, or both. The pages have either torn or been cut to prevent further damage.

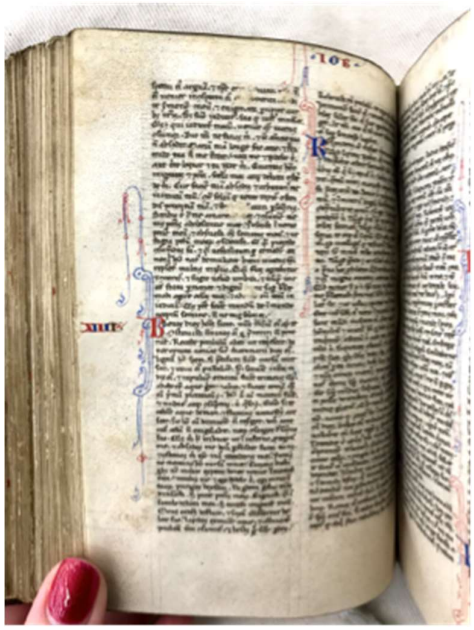


Figure 71: Fol. 135r, which shows areas of ink loss, and the goat hair follicles in the top left.

Numerous pages have patches of ink loss, as can be seen in both Figure 70 and Figure 71. Many pages have blotches, stains and soiling from use - Figure 72 shows what looks like a wax stain, for example.

Figure 72: Cosin V.V.17 fols. 4r and 5v showing damp damage and cut/torn pages, plus a wax stain.

Text layout, ornamentation and rubrics

The bottom margins of the first recto of many quires, of the recto or verso of the first leaf of the second half of some quires, and of a few other leaves, contain horizontal flourishing in red and blue.

Decorated initials herald the start of a new chapter, and there are chapter initials in red and blue. Running-titles, which name the books, are spread across whole openings in alternating red and blue capitals. Marginal chapter-numbers are also in red and blue capitals.[34]

Script and hands

The text is a very neat, small, round textura, written by several scribes, the manner changing noticeably on seven occasions. This is consistent with a workshop approach to manufacture.[35]

Artwork

Artists and painters

It is difficult to discern how many artists might have worked on Cosin V.v.17 due to its formulaic artwork. The only hint that there may be more than one artist involved is that some of the initials use a vibrant pink that is not found in the rest of the artwork, and the initials that do feature this are, on the whole, simpler in conception than the other decorations, containing more plain blocks of colour and using gold, rather than pigment, to colour the initial. An example of this is seen in Figure 73.

Figure 73:The initial from DUL Cosin V.v.17, fol. 239 v. Not that this image also shows the gold loss on the initial, with the pink ground underneath.

[34] Durham University Website, 'Special Collections: DUL MS Cosin V.V.17 Biblia s. Xiii - Durham University', accessed 13 February 2020, https://www.dur.ac.uk/library/asc/theme/medmss/apvv17/.

[35] Durham University Website.

Style of Artwork

Compared to DCL A.II.3, the artwork in DUL Cosin V.v.17 is modest. There are no historiated initials. The decorated initials are striking, but formulaic, and are always blue or orange with the exception of fol. 239 v. All the decorated initials have a gold background or a gold letter-shape. There are smaller and larger plain coloured text initials surrounded by red and blue flourishing, and rubrication in plain red. Red and blue running headings in the top margins and the chapter numbers in the outer margins are not flourished. There is sometimes flourishing as decorative embellishment in the lower margin.

The most impressively decorated pages are fols. 267v and 268r, seen in Figure 74. These pages contain all the features mentioned above and typify the neat and plain but striking blocks of colour that characterise the decorated initials throughout the book.

Figure 74: Fol. 267v and 268r of Cosin V.v.17.

Approach to Painting

Palette

Like DCL A.II.3, DUL Cosin V.v.17 displays a limited palette, and this is exemplified in Figure 74 above. There is a vibrant blue, a vibrant orange and a vibrant green, sometimes accented with thin white lines and dots but otherwise unmodulated. There is also a light brown/pink colour that I will refer to as

brown; again, this is used either by itself or accented with white. There are also a few initials that deploy a more vibrant pink colour. All these colours are outlined in black. There is plenty of gold in the book, as it is deployed in every initial, generally as a background to the decorated initials but occasionally for the letter-shape.

Red and blue are used for text ornamentation and flourishing, and the rubric is written in orange.

Use of Blue

Along with orange, described below, blue is one of the colours that features most often in Cosin V.v.17, being deployed as the main colour of some of the decorated initials, and as infills to others. It is also used in the running headings and text ornamentations, described separately below.

The first folio of the manuscript proper, fol. 3r, is seen in Figure 75 below and shows a decorated initial in blue (albeit sadly damaged as noted above). It is reasonable to suppose that blue was considered the most important colour in this manuscript, given its prominence, and this is supported the fact that the blue is lapis lazuli – the most expensive pigment by far, as described in chapter two.

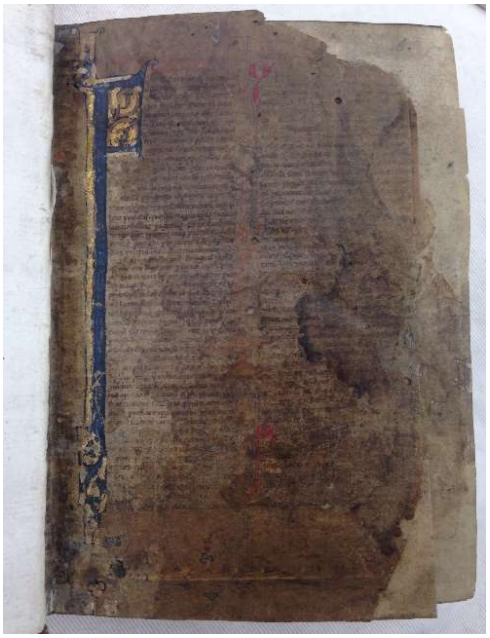


Figure 75: Fol. 3r of Cosin V.V.17, showing both the damage and what remains of the blue decorated initial.

Spectra

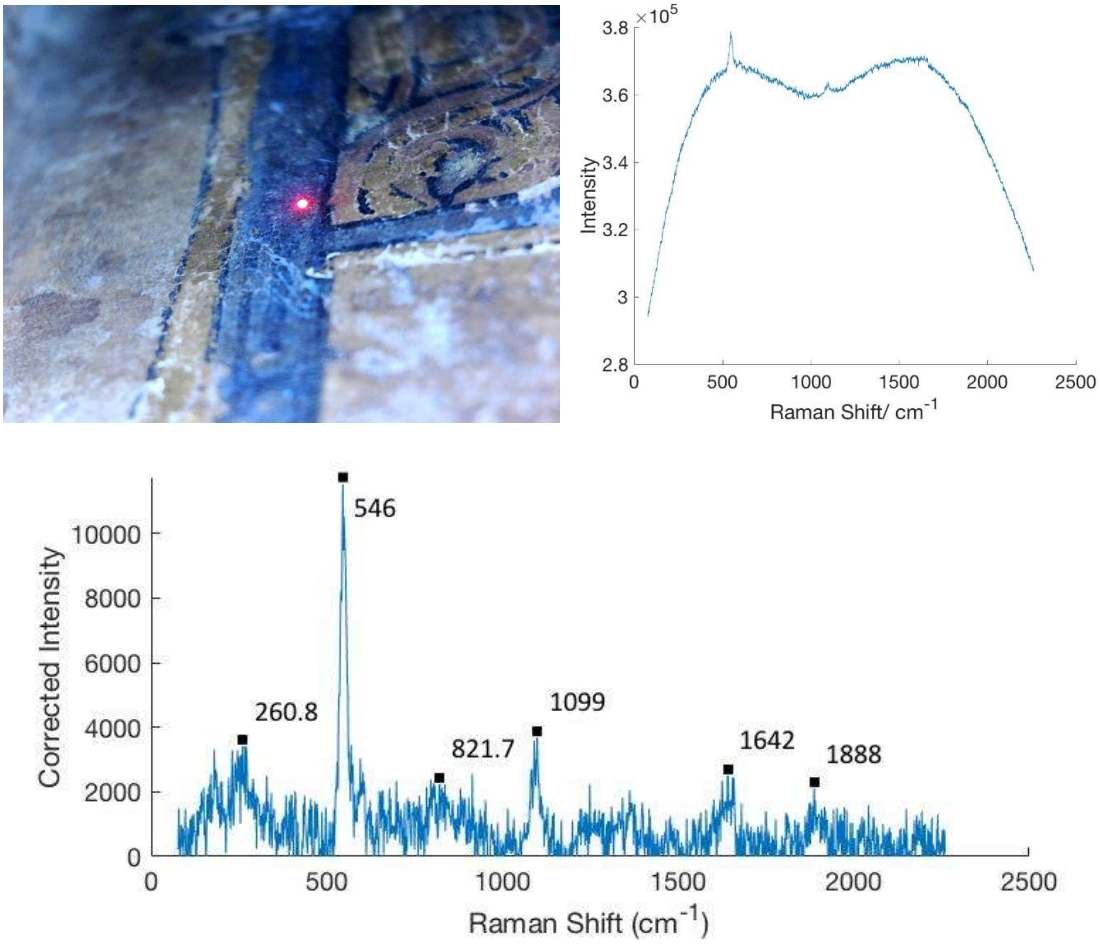


Figure 76: (top left) The spot on fol. 3r that gives the raw Raman spectrum (top right), and the processed spectrum (below).

The spectrum obtained for the blue employed here is lapis lazuli, with peaks at 261, 546, 822 and 1099 cm^{-1}, confirmed by published data which state that the peaks are at 258, 548, 822 and 1096 cm^{-1}.[36]

The decorated initial on fol. 267v, as shown in Figure 77 is also lapis lazuli, as confirmed by the Raman spectrum with peaks at 252, 550, and 837 cm^{-1} which also concurs with the published data.

[36] I. M. Bell, R. J. Clark, and P. J. Gibbs, 'Raman Spectroscopic Library of Natural and Synthetic Pigments (Pre-Approximately 1850 AD)', *Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy* 53A, no. 12 (15 October 1997): 2159–79.

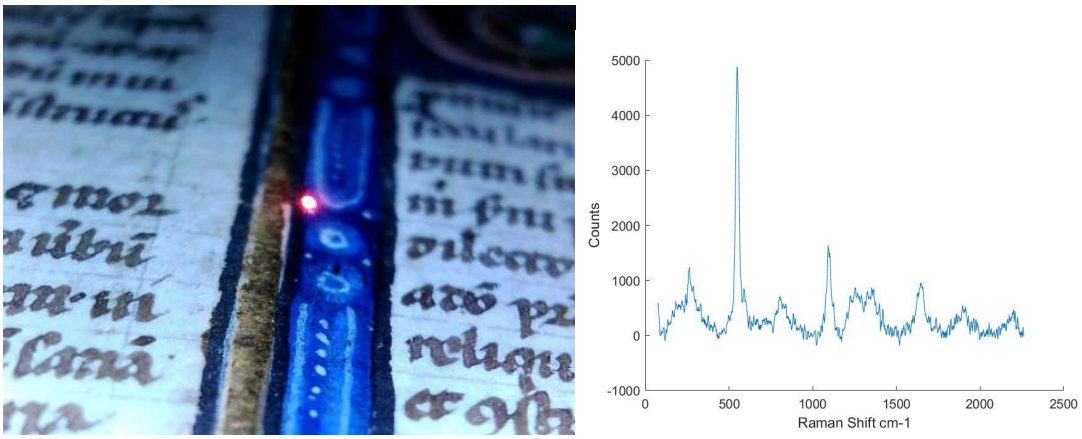


Figure 77: (left) The spot of the initial on fol. 267v where the Raman spectrum (right) was obtained.

FORS was also used on the decorated initial on fol. 267v, and the spectrum is shown in Figure 78. The absorbance maximum is 616 nm, which is broadly consistent with published data stating that the absorbance maximum of lapis lazuli is 600 nm. There are no characteristic absorption bands of azurite present in the FORS spectrum (at 2281 and 2350 nm), which would indicate the presence of azurite.[37]

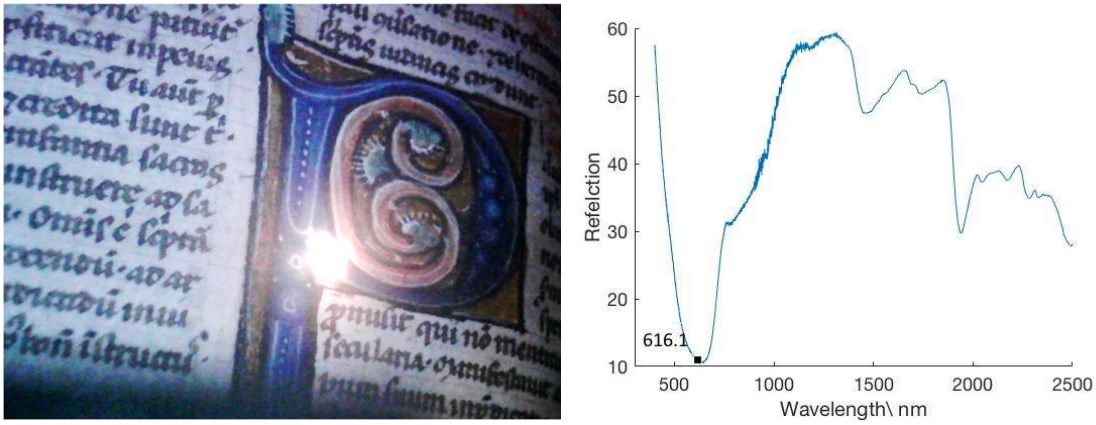


Figure 78: (left) The spot on fol. 267v where the FORS spectrum was taken and (right) the FORS spectrum obtained - that of lapis lazuli.

Use of Orange

As exemplified in Figure 74, orange is one of the colours used as the main colour in the decorated initials in Cosin V.v.17. As Figure 79 shows, this is red lead, confirmed by the Raman spectrum, which

[37] Delaney et al., 'Use of Imaging Spectroscopy, Fiber Optic Reflectance Spectroscopy, and X-Ray Fluorescence to Map and Identify Pigments in Illuminated Manuscripts', p. 97.

shows peaks at 127 and 548 cm^{-1}. This is consistent with published data for red lead that reports peaks at 121 and 549 cm^{-1}.[38]

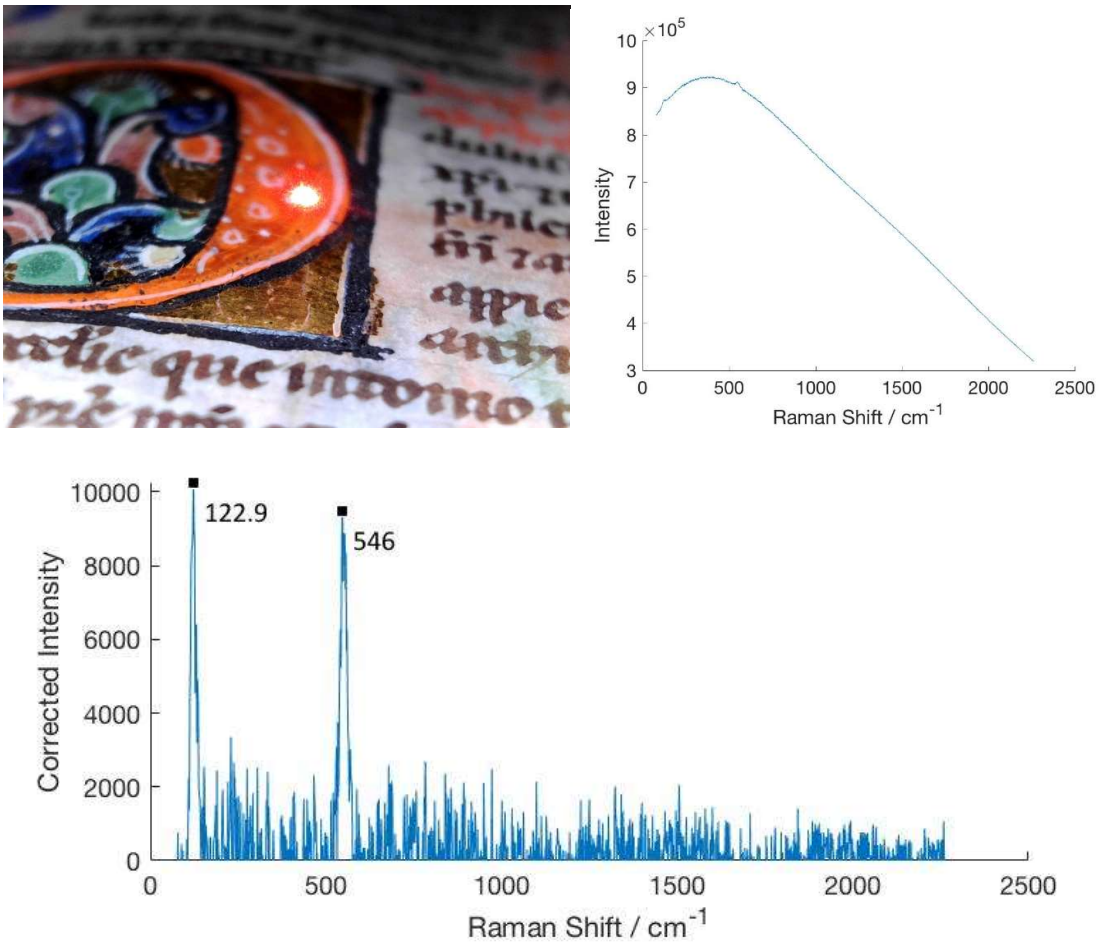


Figure 79: (top left) The spot on fol. 268r where the raw Raman spectrum (right) was obtained, and (below) the processed spectrum.

The FORS spectrum of the orange pigment on this initial also confirms that this is red lead, by its inflection point at 568 nm, which is consistent with published data which state that the inflection point is 565nm.[39]

[38] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

[39] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

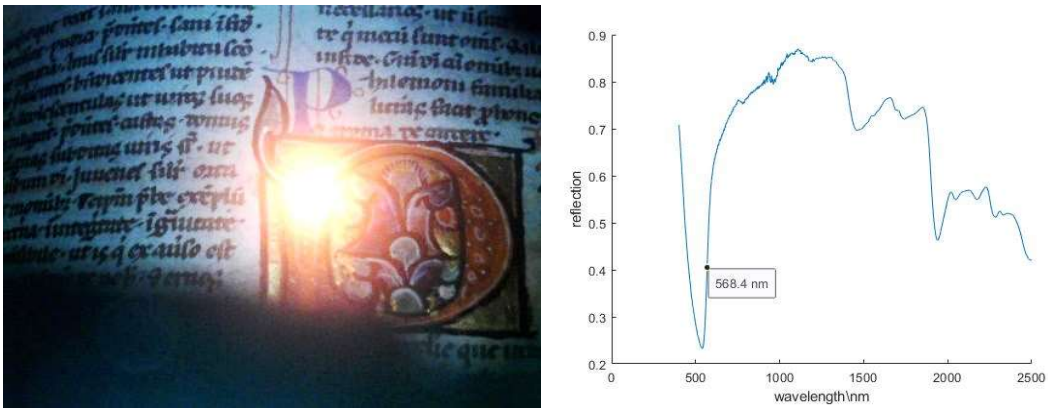


Figure 80: (left) The spot on 268r where the FORS spectrum (right) was obtained.

As well as being the main colour for decorated initials, orange was also used as an infill for blue initials. The orange infill in Figure 81 is shown to be red lead. The red lead peaks at 128 and 555 cm^{-1} correspond to the published data mentioned above, whilst the peaks seen at 228, 321 and 394 cm^{-1}, are also consistent with published data for red lead that has the peaks at 223, 313 and 390 cm^{-1}.

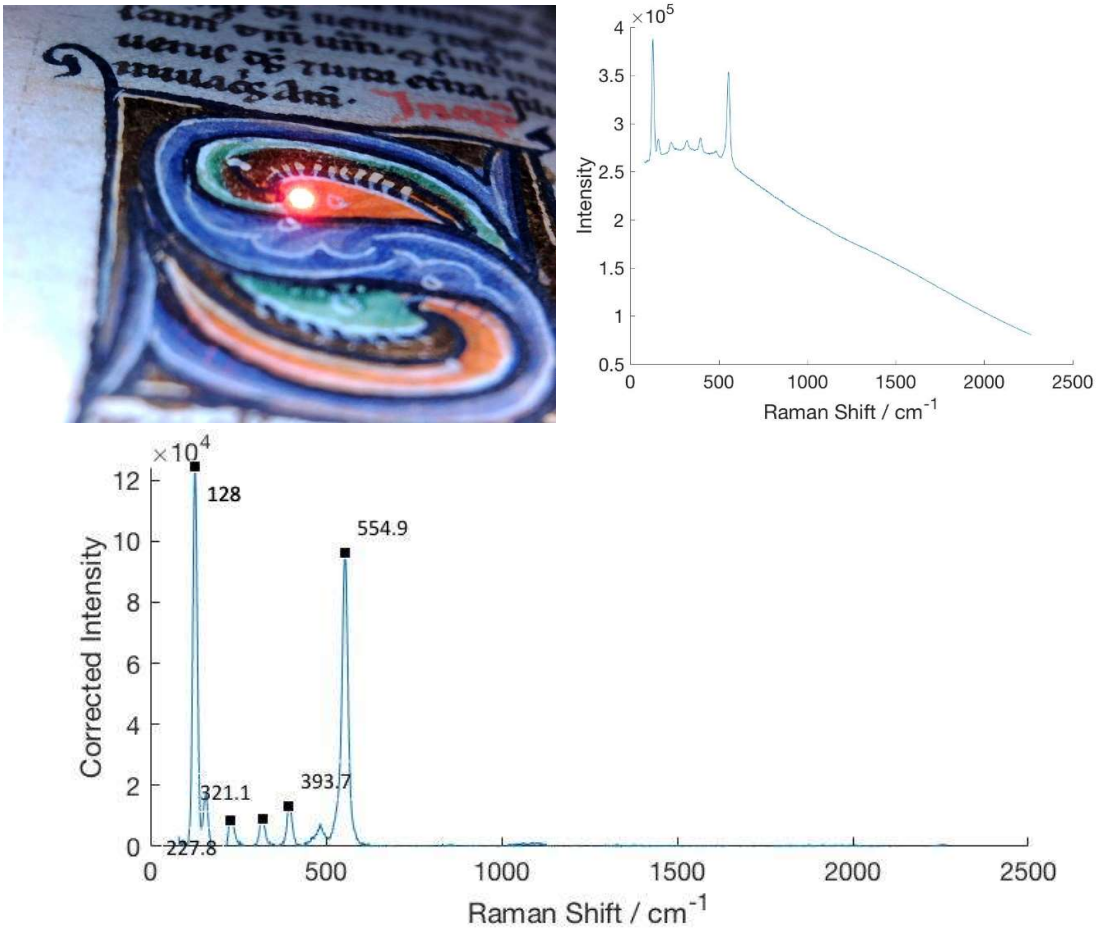


Figure 81: (top left) The spot on fol. 286v where the raw spectrum (top right) was obtained, and (below) the processed spectrum.

Use of Green

Green is used sparingly in the manuscript, occurring only as foliate decoration in and around decorated initials, as seen in Figure 82, for example. There are no initials coloured predominately in green.

Spectra

Figure 82: Cosin V.v.17 Fol. 267 v.

On fol. 267v, Figure 82, the green foliate decoration was examined with both Raman spectroscopy and FORS. The results are interesting and could be interpreted in different ways.

One explanation is that the Raman spectrum, seen Figure 83, shows two peaks that identify the presence of lapis lazuli, 546 and 1098 cm^{-1}. The other peak, at 748 cm^{-1}, is not a lapis lazuli peak, and, at the 633 nm laser wavelength, does not correspond to any known pigment. As the pigment is green, not blue as would be expected from lapis lazuli, it can be reasonably expected that the peak at 748 cm^{-1} is from a yellow pigment, as yet unidentified, meaning the pigment can be identified as vergaut, a green made from a mixture of a blue and a yellow pigment.

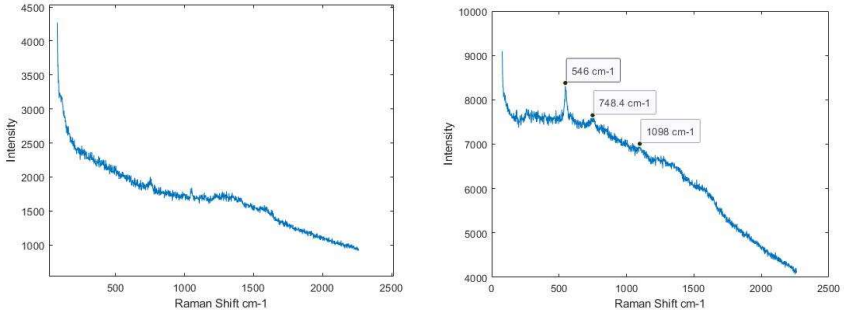


Figure 83: (top) The spot on fol. 267v examined by Raman spectroscopy and (below) the raw Raman spectrum obtained (left) and processed (right).

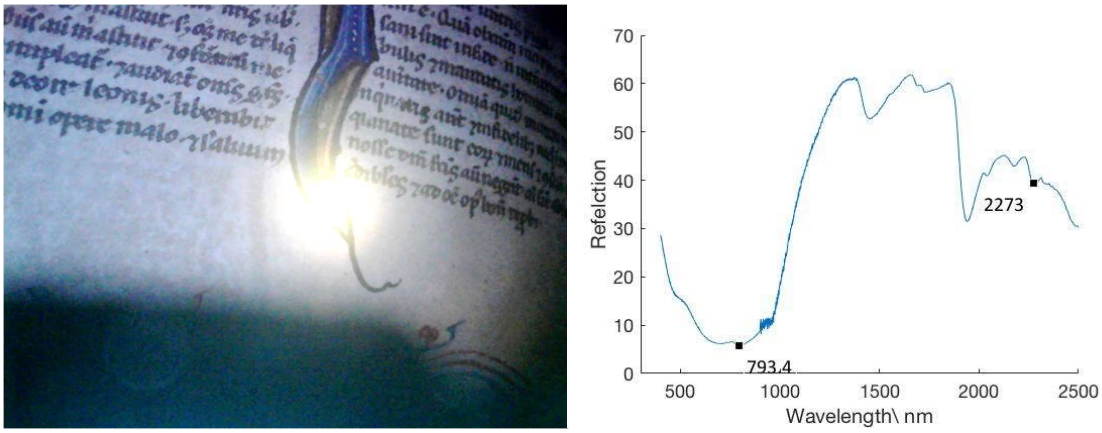


Figure 84: (left) The spot on fol. 267v examined by FORS, and (right) the spectrum obtained.

Use of black

Black is used to outline the colours in every decorated initial; an example can be seen in the microscopy image in Figure 85. The black pigment has been identified by Raman spectroscopy as carbon or lamp black. In this spectrum, broad peaks can be seen at 1348 and 1601 cm^{-1}. These are

consistent with published data for carbon, which state that the Raman peaks are at 1348 and 1598 cm^{-1}. [40]

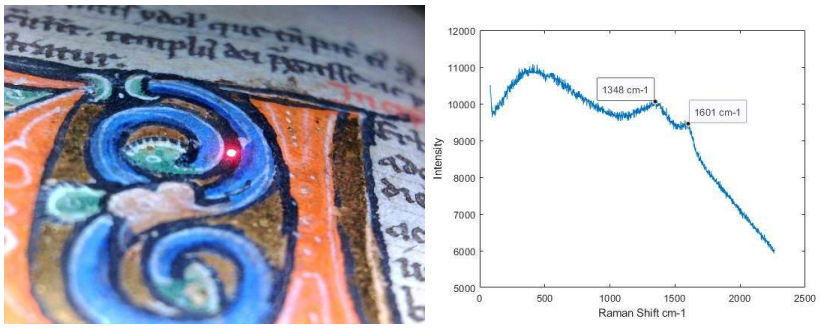


Figure 85: (left) The spot on fol. 225v where the black pigment was examined, and (right) the labelled raw Raman spectrum

Use of pink

As mentioned above, there is a vibrant pink that is used in only a few initials in the second half of the manuscript, as a background to gold initials. The pink background on fol. 168v, seen in Figure 86, was examined with Raman spectroscopy. However, no peaks in the spectrum were obtained due to fluorescence, which in itself points to the pink being from an organic source.

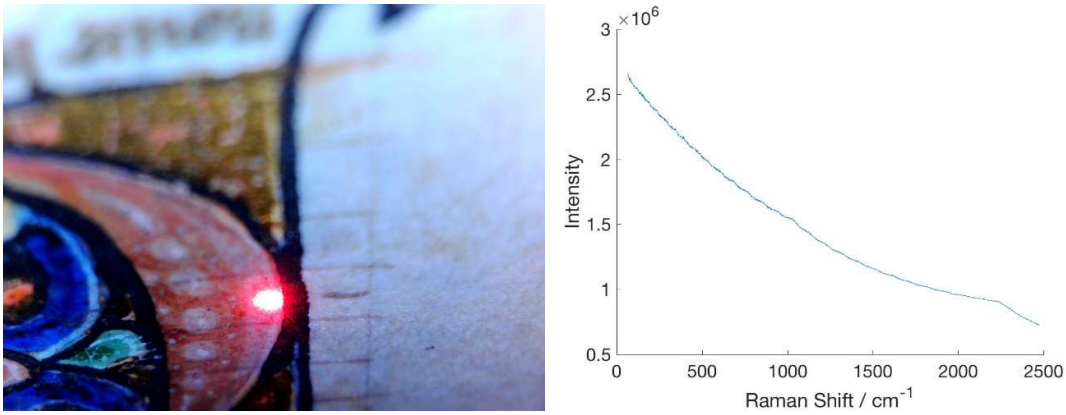


Figure 86: The spot examined on Cosin V.V.17 fol. 168v which returned (left) the area of pink examined and (right) the raw spectrum obtained.

[40] M.C. Caggiani, A. Cosentino, and A. Mangone, 'Pigments Checker Version 3.0, a Handy Set for Conservation Scientists: A Free Online Raman Spectra Database', *Microchemical Journal* 129 (November 2016), p. 127.

A FORS spectrum of the pink was obtained from fol. 168r, as can be seen in Figure 87. This shows an inflection point at approximately 600 nm and an absorbance maximum of 560 nm. The 600 nm inflection point is consistent with published data which state that 600 nm is red lead. It could be that the paint contains some red lead; however, red led is usually a more orange or red colour, so if it is present in this pink, it is likely to be as one component in a mixture. The circumstance that the Raman spectrum did not give a red lead spectrum does not rule out its presence - the red lead signal may have been swamped by fluorescence, as previously mentioned.[41] In addition, the FORS spectrum shows an absorbance band at 1447 nm, indicative of white lead.[42] This would suggest that the pink is a mixture of red lead and white lead, with or without other components.

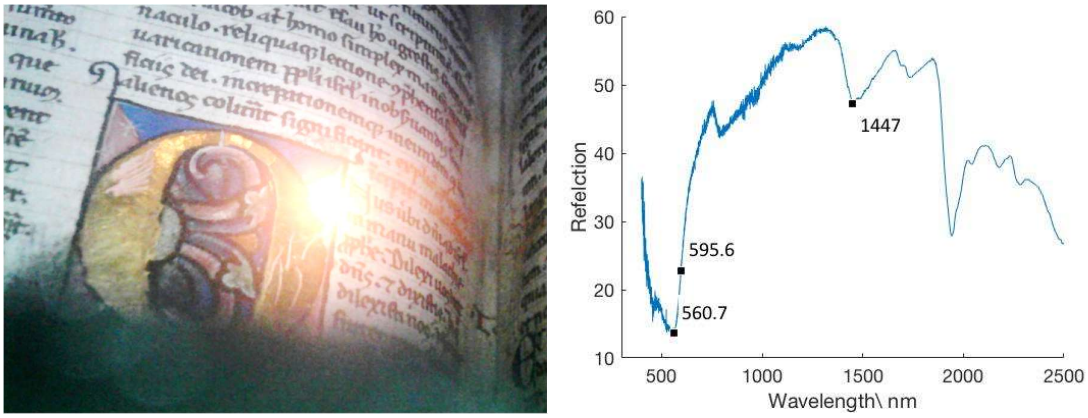


Figure 87: Cosin V.v.17 fol. 240r (left) the spot on the vibrant pink examined, and (right) the FORS spectrum.

Furthermore, the absorbance maximum of 560 nm is exactly that of Brazilwood. Brazilwood, being organic, is a dye and usually used as a glaze. In this case, when examined by eye, the pink appears to be a block of solid colour - i.e., a mixture of pigments and/or dye, applied to the page in one go, rather than a substrate of a pigment with a dye glaze. That the FORS spectrum would pick out three pigments and identify them separately by means of inflection point, absorbance maximum and absorbance

[41] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

[42] Delaney et al., 'Use of Imaging Spectroscopy, Fiber Optic Reflectance Spectroscopy, and X-Ray Fluorescence to Map and Identify Pigments in Illuminated Manuscripts', p. 97.

band is unlikely, as a mixture of components is likely to alter the whole spectrum (discussed earlier, in Chapter 3).

Figure 88: The initial on Cosin V.v.17 fol. 239v clearly showing the gold loss.

On fol. 139v, as seen in Figure 88, the gold leaf has been scratched away to reveal the pale pink gesso underneath. Pink, red or yellow under-layers were often used under gold leaf to give it a warmer hue and to mitigate the effect of any losses. The area underneath the scratch was large enough to allow the pigment revealed to be analysed by Raman spectroscopy, and the spectra are shown in Figure 89. The peaks at 128 and 555 nm are consistent with published data for red lead, but the peak at 1019 nm is not a red lead peak. Given that red lead is usually a vibrant orange or red colour, whereas this gesso is a pale pink, it might be assumed that the gesso contains a mixture of pigments, with a white colourstuff amongst them. The peak at 1018 cm^{-1} could be gypsum (calcium sulfate), therefore.[43]

[43] Caggiani, Cosentino, and Mangone, 'Pigments Checker Version 3.0, a Handy Set for Conservation Scientists', p. 126.

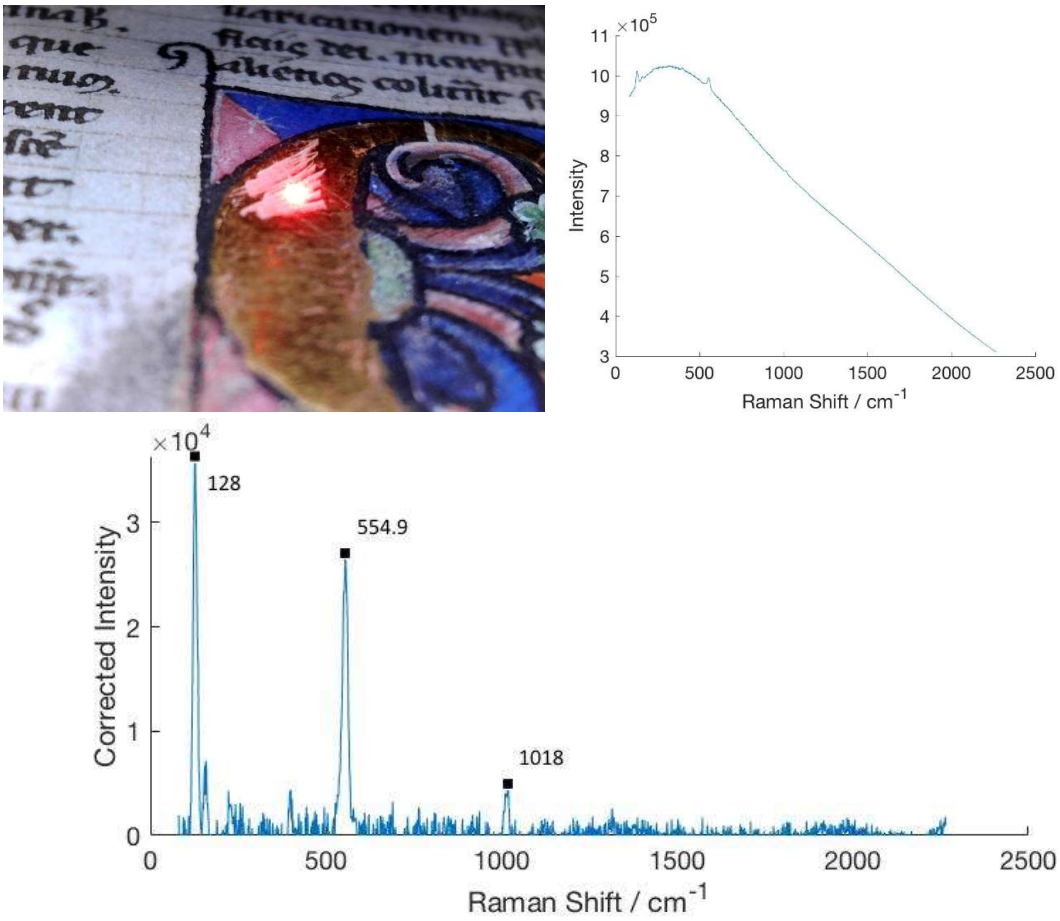


Figure 89: (top left) The area on fol. 239v examined, (top right) the raw spectrum obtained, and (below) the processed spectrum.

Use of brown

Figure 90 shows the decorated initial on fol. 225v with a dusky brown at its centre. Like pink, brown is often a difficult colour to analyse as it is either a mixture of compounds or comes from organic sources. In this instance, the spectrum does not reveal any information as to the nature of the pigment.

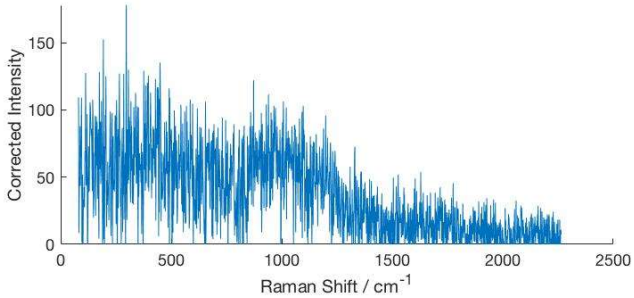


Figure 90: (top) A close-up image of the initial on fol. 225v, showing brown in the centre. (Below left) the spot on fol. 225v where the brown was examined, and (right) the raw Raman spectrum obtained.

Use of White

Figure 91: A photomicrograph of the initial from fol. 265 v.

White is used in most of the initials examined, but never as a block of colour, always as a highlight or to modify the tone of another colour. As can be seen in Figure 91, white is used in lines and dots to provide decorative articulation to the blue, brown, and pink and to highlight the green; it is also deployed inside the black outline on top of the gold leaf. Given how small are the quantities in question, it was difficult to obtain a pure white lead spectrum from them. However, as Figure 92

shows, a spectrum of white lead and lapis lazuli was obtained from the white line painted on the blue infill.

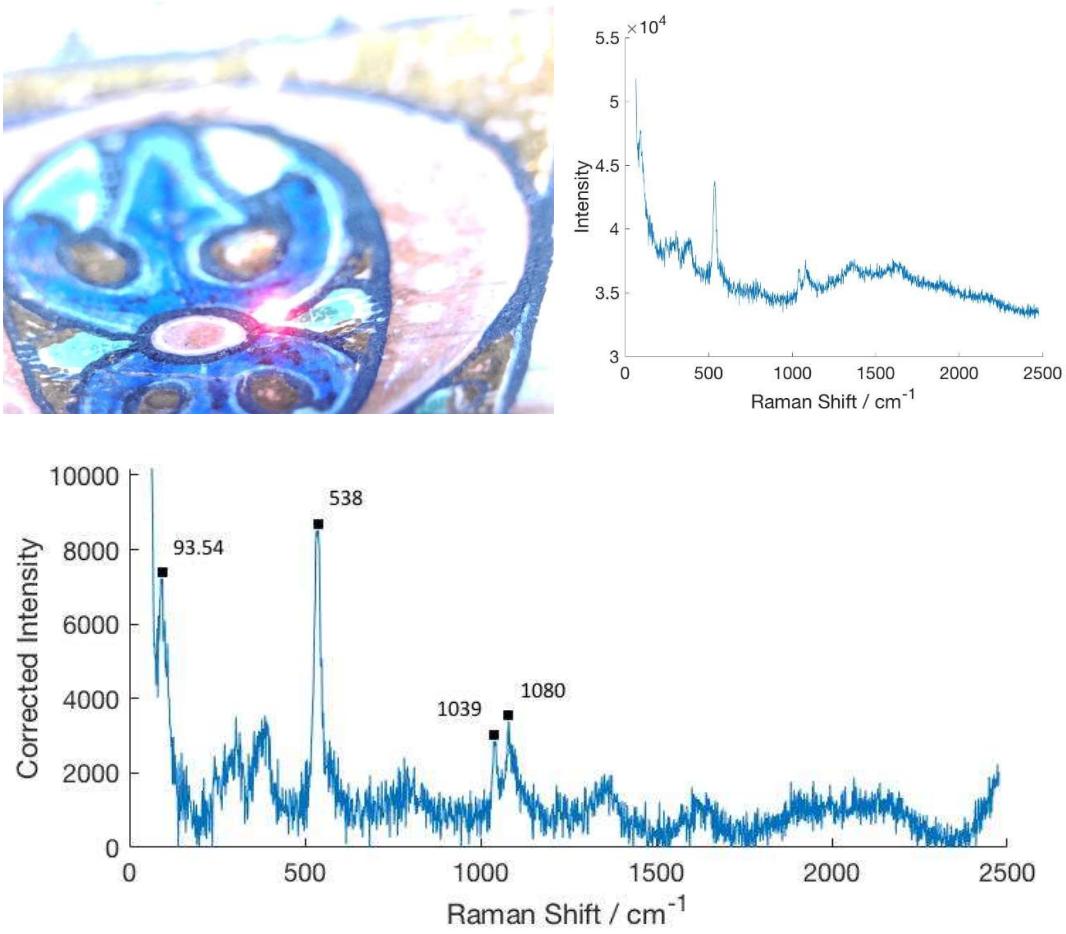


Figure 92: Cosin V.v.17 fol. 168v (left) the spot on the white line where the raw Raman spectrum (top right) and the processed spectrum (bottom) were obtained.

The Raman peaks at 104 cm^{-1} and 1049 cm^{-1} are consistent with the published data for white lead, which have the peaks at 104 cm^{-1} and 1050 cm^{-1}, whilst the peaks at 548 cm^{-1} and 1090 cm^{-1} are consistent with data for lapis lazuli, which state that the peaks are at 550 cm^{-1} and 1095 cm^{-1}.

Use of Gold

Figure 93: Cosin V.V.17 fol. 65v (left) and 72v (right).

Gold is utilised in every initial in the manuscript and was applied in leaf form and then burnished. As exemplified in Figure 93, gold was often used as infill behind a blue or orange coloured initial. The leaf is still intact in Figure 88, further above, and wrinkles can be seen in the surface, which would not happen if the gold were shell gold. As discussed in chapter two, gold does not produce a Raman spectrum as it is too reflective. A FORS spectrum was obtained from fol. 168v, as seen in Figure 94. The spectrum obtained has an inflection point at about 650 nm and no obvious absorbance maximum. This is not consistent with any published library data, which suggests that gold has an inflection point of 510 nm. In this manuscript, the gold is so obviously gold leaf, that the discrepancy must be put down to the reflective nature of the gold.

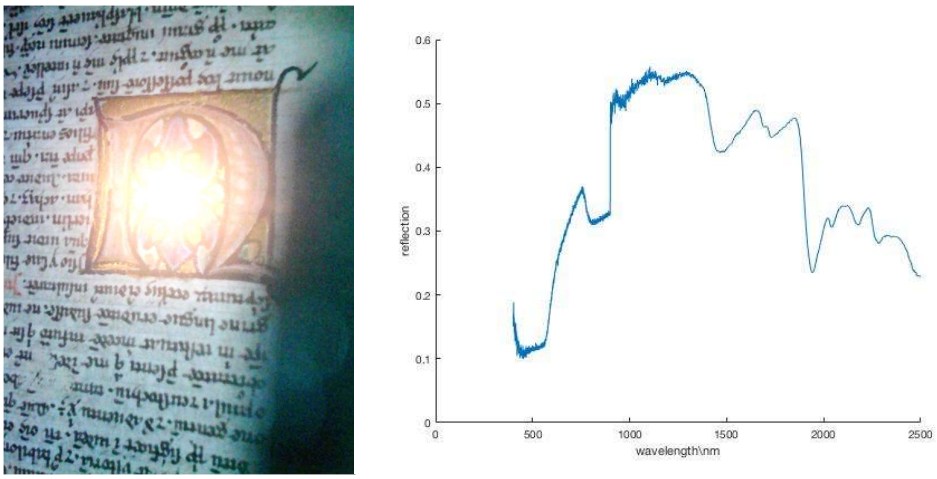


Figure 94: (left) The spot on the initial on Cosin V.v.17 fol. 168v where the FORS spectrum (right) was obtained. Note that the step in the spectrum at about 750 nm is due to an error in the calibration of the software.

Text and text ornamentation

Text

As described above, the text is a neat Textualis written in black ink, as seen in Figure 102. A Raman spectrum of this text, shown in Figure 95, gives no peaks, suggesting that the ink does not contain carbon, and is, therefore, gallotannic ink. However, to be conclusive, a FORS spectrum would be required. As the writing is so small no suitable FORS spectrum was able obtained - the spot area always included more than 50% parchment.

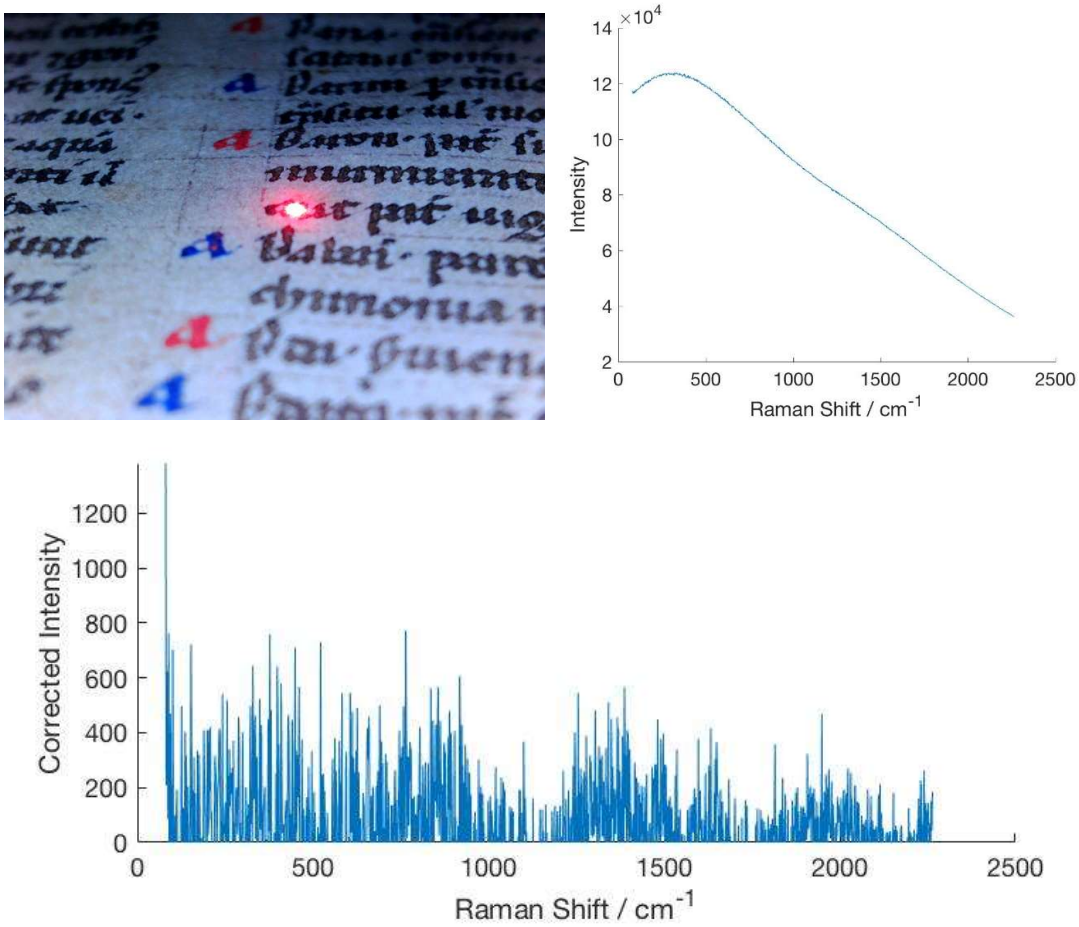


Figure 95: (top left) The spot on Cosin V.V.17 fol. 292r where the Raman spectrum was taken, (top right) the raw spectrum obtained and (bottom) the processed spectrum.

Text initials

Figure 96: (left) A red chapter or text initial on fol. 225v and (right) a blue chapter initial.

Chapter initials alternate between red and blue. Figure 96 shows close-ups of both colours of text initial - the red is vermilion, and the blue is lapis lazuli, as can be seen in the spectra below in Figure 97. Lapis lazuli can be determined by the peaks at 552, 1099 and 1640 cm^{-1}, whereas vermilion can be determined by the peaks at 259 and 350 cm^{-1}, each consistent with published data.

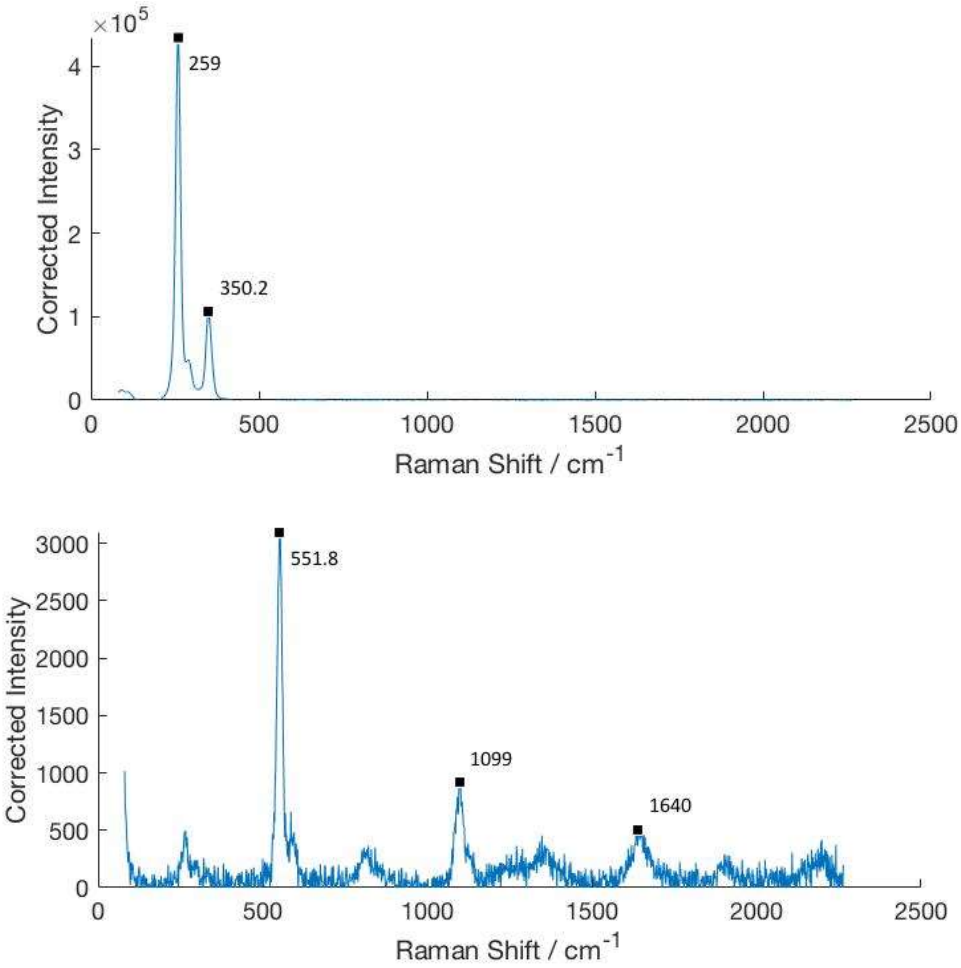


Figure 97: (top) The Raman spectrum of the red chapter initial on fol. 225v, and (bottom) the blue chapter initial.

Rubric

The rubric throughout the manuscript is an orange-red colour, especially when compared to the vibrant red of the text initials. Figure 96 above shows a text initial and the rubric next to one another: to the eye they look as if they might be different pigments, as the colours are quite different. It is surprising, therefore, to discover that the red of the rubric is vermilion like the verse initials, as shown in the Raman spectra in Figure 98. However, the intensity of vermilion signal obtained differed from one to the other. The more vibrant red vermilion in the text initial gives a signal an order of magnitude bigger than the more orange-red in the rubric. This could indicate that the rubric contains a mixture

of pigments, one of which is vermilion, or that the vermilion was here liquefied with a different binder, one which has affected its colour. Vermilion is a pigment that often gives a very strong Raman spectrum signal, so it is possible that the vermilion signal is swamping any other signals (such as red lead) that might be obtained from the more orange-red.

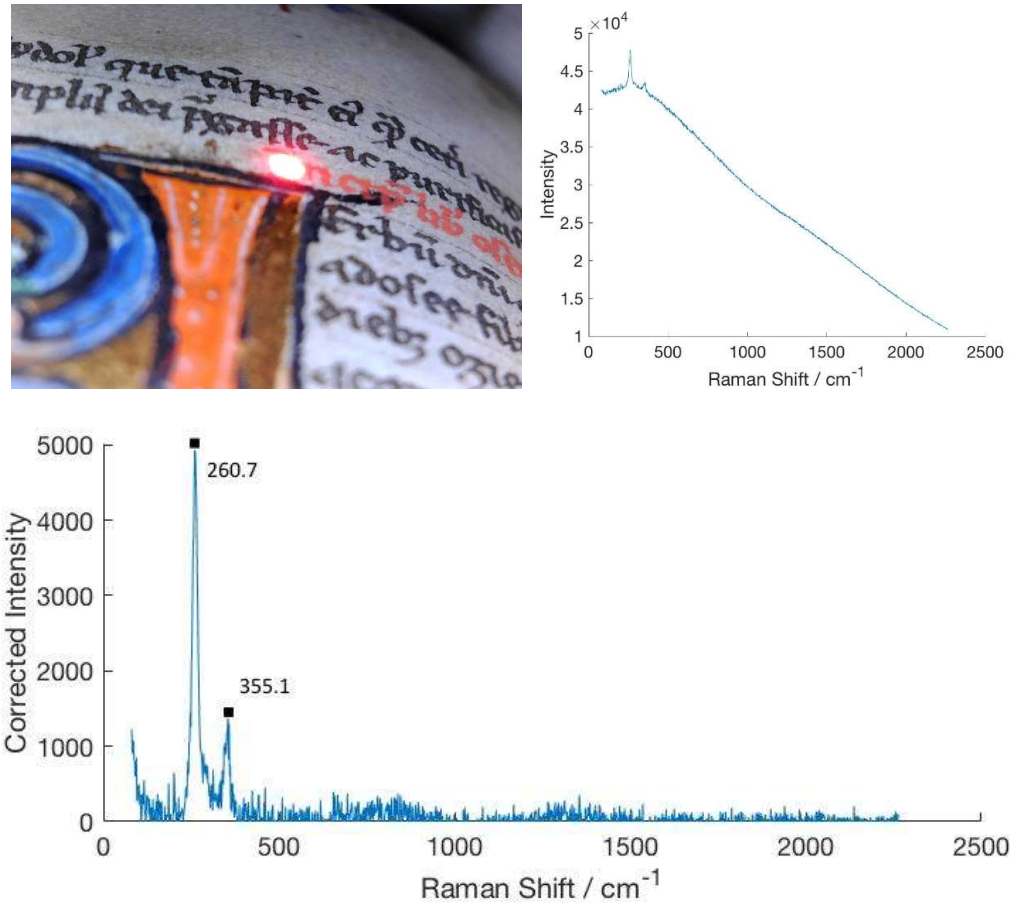


Figure 98: (top left) The spot on fol. 225v where the rubric was examined, (top right) the raw spectrum obtained, and (below) the processed spectrum.

Flourishing

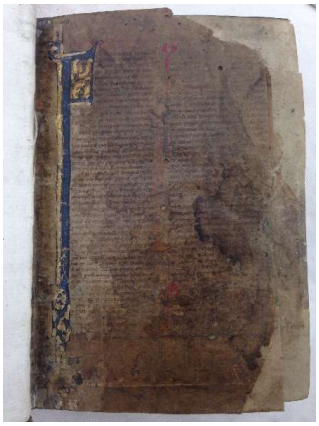


Figure 99: Cosin V.v.17 fol. 3r

The red and blue of the flourishing that adorns the book are vermilion and lapis lazuli, respectively. It is interesting that despite fol. 3r being in very poor condition due to water damage and overuse (see Figure 99), the Raman signal of both substances can still be ascertained.

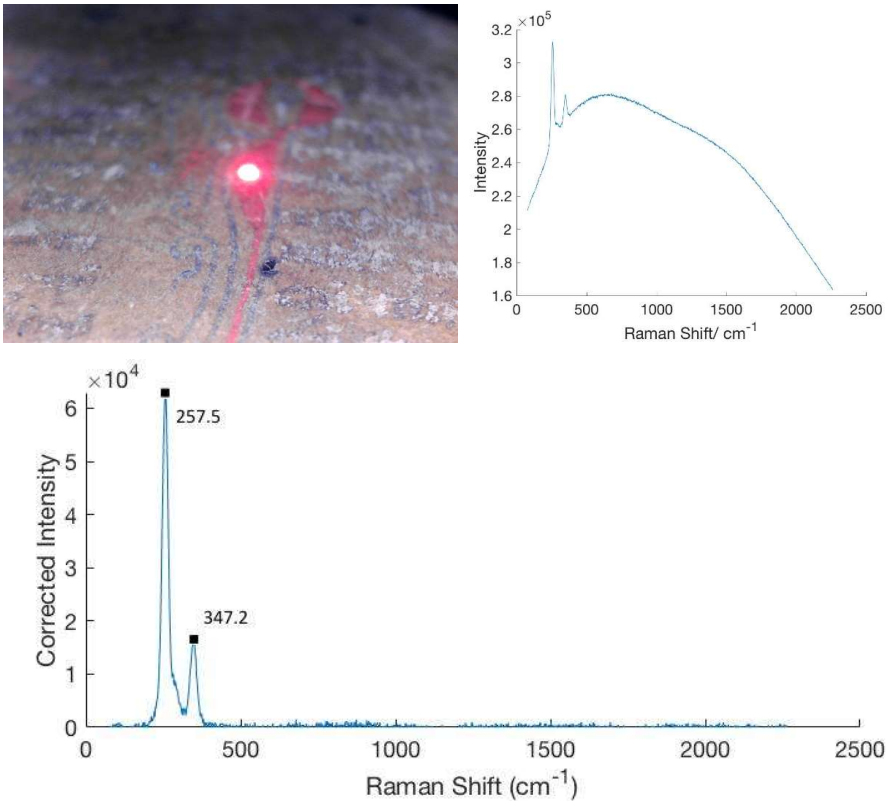


Figure 100: (top left) The spot on Cosin V.v.17 fol. 3 where the raw spectrum (top right), and the processed spectrum (below) were obtained.

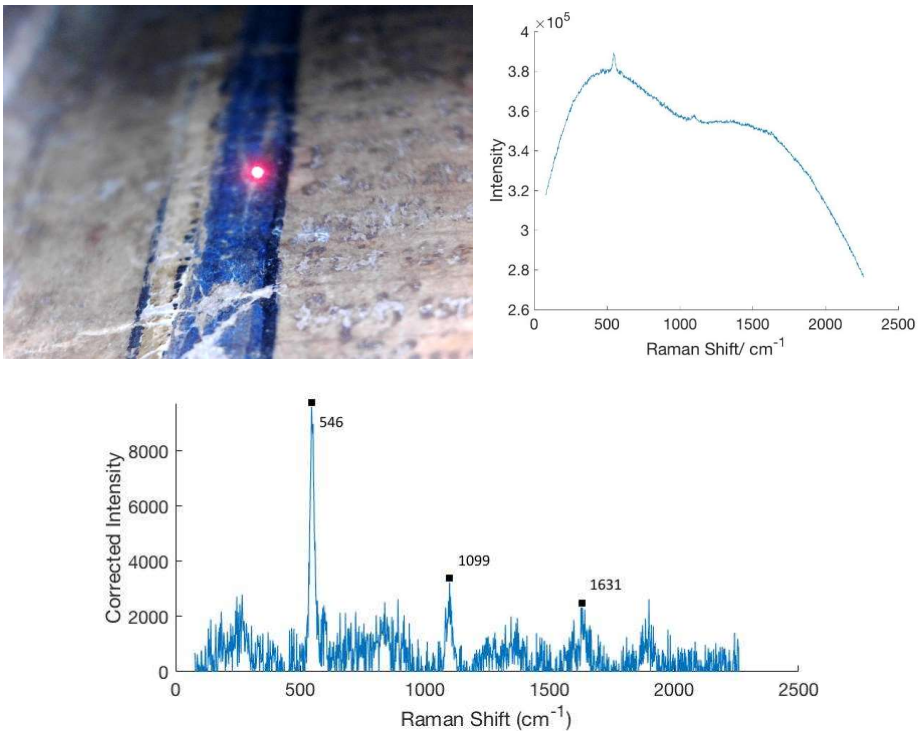


Figure 101: Cosin V.v.17 fol. 3r showing (top left) the spot where the raw lapis lazuli spectrum (top right), and processed lapis lazuli spectrum (bottom) were obtained.

Running heading /chapter headings

Index

Figure 102: Cosin V.V.17 fol. 292v - the Index of Hebrew names.

A common and standard feature - the index of Hebrew names on fol. 292v - is an addition to the core bible text and may have been completed by a different scribe and/or artist. However, as can be seen in Figure 103, the fact that the index starts on the same folio as the bible text ends suggests that work on the index was completed in collaboration with the scribe of the main text, rather than the index of names being worked on completely separately.

The index is demarcated with red and blue index initials, and these are lapis lazuli and vermilion as expected. The spectra of these can be seen in Figure 103 and Figure 104.

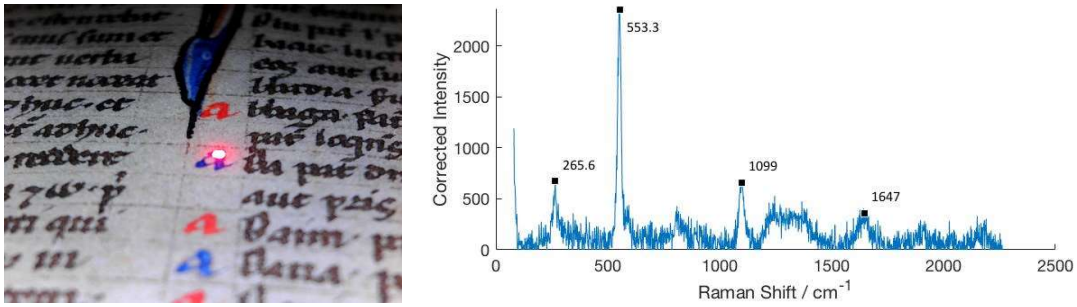


Figure 103: (left) The spot on Cosin V.v.17 fol. 292v where the lapis lazuli spectrum (right) was obtained.

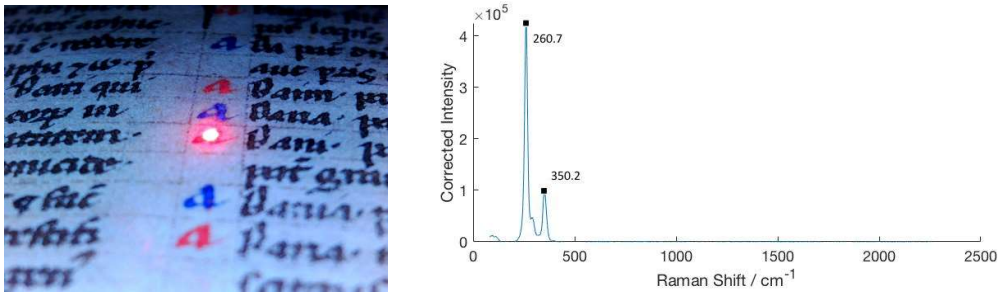


Figure 104: (left) The spot on Cosin V.v.17 fol. 292r examined by Raman spectroscopy, and (right) the vermilion spectrum obtained.

Further Comments on the Palette as a Whole

To summarise, the colourants deployed in this manuscript are lapis lazuli, vermilion, white lead, red lead, gypsum, carbon, oak gall ink and potentially Brazilwood and malachite. Gold, classed as a metal, was also employed. These are all pigments that are consistent with what is known so far about pigment use in the thirteenth century. The potential identification of Brazilwood is also interesting - being organic and thus not giving a Raman spectrum means its use is difficult to ascertain, and furthermore, the fact that it is often employed in a mixture or as a glaze over another pigment means that it is not examined in isolation, again making its usage difficult to ascertain.

Chapter Four Part B

Analysis of DUL Cosin V.v.18, DCL A.IV.30 and DCL A.IV.37

Durham University Library Cosin V.v.18

Description and Provenance

Like DUL Cosin V.v.17, Cosin V.v.18 is a pocket-sized Paris Bible made in the thirteenth century. It has been suggested that the inclusion of Psalms and the style of the artwork, discussed further below, mean that this manuscript was made in Northern France. It measures 132 mm by 88 mm and has 421 leaves and two flyleaves.[1]

The Manuscript contains the Bible in the usual order, although the books of Nehemiah, Judith, Esther, Job and Hosea to Haggai, i.e., most of the books of the Minor Prophets, are not included. Several books of the Bible (including Genesis, Exodus, Psalms and others) are incomplete - in these cases, the books ether start imperfectly (lacking verses at the beginning) or finish abruptly (lacking verses at the end) almost certainly the results of losses due to wear and tear.[2]

Before each book is the common set of prologues as listed in *Medieval Manuscripts in British libraries Volume One*, and a rubric to act as a signifier in the text. Baruch's sermon and Jeremiah's letter have particularly long rubrics.[3]

Following the Bible text, the alphabetised list of Hebrew names, as described by Stegmüller, is appended.[4] Again, the list is incomplete, the last 61 entries from A and all entries from B except three are missing, for example, which would amount to three folios.[5]

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[1] Durham University Special Collections. 'Special Collections : DUL MS Cosin V.V.18 Biblia s. Xiii - Durham University', accessed 24 March 2020, https://www.dur.ac.uk/library/asc/theme/medmss/apvv18/.

[2] 'Special Collections : DUL MS Cosin V.V.18 Biblia s. Xiii - Durham University', accessed 24 March 2020, https://www.dur.ac.uk/library/asc/theme/medmss/apvv18/; N. R. Ker, Ian Campbell Cunningham, and Andrew G. Watson, *Medieval Manuscripts in British Libraries* (Oxford : New York: Clarendon Press ; Oxford University Press, 1969).

[3] 'Special Collections : DUL MS Cosin V.V.18 Biblia s. Xiii - Durham University'; Ker, Cunningham, and Watson, *Medieval Manuscripts in British Libraries*.

[4] F. Stegmüller, *Repertorium Biblicum Medii Aevi*, 1950.

[5] 'Special Collections : DUL MS Cosin V.V.18 Biblia s. Xiii - Durham University'; Ker, Cunningham, and Watson, *Medieval Manuscripts in British Libraries*.

Later additions to the manuscript include a schedule of Old Testament canticles and when to use them added in the later thirteenth century. A list of lections, epistles and gospels for Mass, Christmas and Lent, was added in the fourteenth century in an English hand. There are some sixteenth-century annotations, notably Ave Maria in English on fol. 265.

The book contains a fifteenth-century caution-note referencing Cambridge on fol. 419v, indicating that the book was pawned there and was thus circulating in university circles. On fol. 420, in the seventeenth century "William Wilkingson, his booke" was written, and "Geo. Davenport... 1665" inscribed on a flyleaf, as shown in Figure 1, attest to its later provenance. George Davenport (d.1677) was a chaplain to Bishop Cosin who, like Cosin, also collected manuscripts. His collection was left to Bishop Cosin's Library, where it still remains - as its shelf-mark reminds us.

Figure 1: Cosin V.v.18 flyleaf showing George Davenport's inscription, 1665.

Codicology

Quire formation

The pocket-sized nature of the book and its current tight binding make systematic collation impracticable; however, such quires as can be assessed appear to be 24s or 26s.

Parchment and ruling

Like Cosin V.v.17, the parchment of Cosin V.v.18 is very thin, measuring only 0.05 mm thick with the flesh and hair sides indistinguishable from one another - likely an effect of the severe processing that

some parchment underwent - discussed further in chapter two. This technology allowed the parchment to become thin enough to accommodate 421 leaves and still be pocket-sized.

As all the edges to this manuscript have been cropped, there is no evidence of pricking. The text block of the main bible test measures 92 mm by 62 mm with two columns per page with 49 lines in each. The list of Hebrew Names has a text block measuring 100 mm by 68 mm with 53-56 lines. All lines are ruled in brown.

Despoliation

As mentioned above, all the edges to this manuscript have been cropped, likely during the re-binding that was done in the 19th century. Fols. 206 and 207 are stained and partly torn whilst several folios have liquid damage. Some small tears in fol. 107 and fol. 305 have been repaired.

Text layout, ornamentation, and rubrics

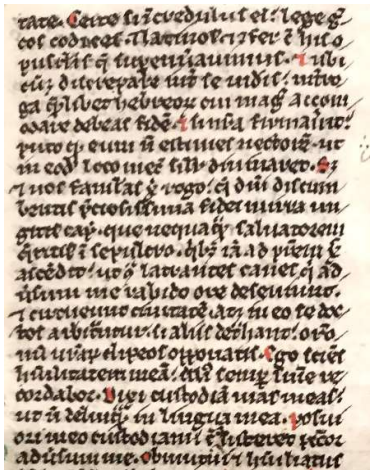

Figure 2: A selection of the text showing the small red strokes on the text capitals, Cosin V.v.18 fol. 94r.

A red stroke is used to highlight capital letters throughout the Bible, as seen above in Figure 2. Alternate Red and blue text initials one line high are used in Psalms, and the appended the list of Hebrew names. The same red and blue alternations two lines high are used to denote chapters and sub-divisions in the list of Hebrew names and these are flourished with the other colour. Prologues to the books of the Bible are treated similarly but usually with a three-, four-, or very occasionally a five-line high initial and alternate colour flourishing. Running titles that name books across an opening are in alternating red and blue capitals. Chapter numbers in the margins are similarly decorated.

Decorated initials, at least five lines high, are used to signify the books of the Bible, with some exceptions, and to signify some Psalms, and the list of Hebrew Names. The artwork of these initials is discussed below.

Script and hands

The very small script is Gothic Textura, written very proficiently, as shown in Figure 2.[6] It was not possible to determine the number of hands.

Artwork

Whilst the decoration in Cosin V.v.18 is modest compared to that of Cosin V.v.17, it is certainly deftly executed. Pink and blue initials, which generally alternate, are patterned with white dots and outlined in black. The animals and foliate forms that adorn the initials are filled with blue of differing shades, pink, grey, brown, orange, or yellow-brown, and are embellished with white. There was no gold seen in the manuscript.

The catalogue description for Cosin V.v.18 suggests that the artwork is consistent with the style of the Amiens Atelier, as typified by Robert Branner.[7] As can be seen in Figure 3, the initial 'I' that Branner uses to exemplify artwork from the Amiens Atelier, although slightly more angular and intricate than the more curvy simpler design from Cosin V.v.18, is very similar to that in the latter. Both initials use pink ground with looping stems highlighted in white that end in an animal face or a foliate form. This would suggest that the Amiens Atelier is a strong possibility for the origin of this manuscript.

[6] Durham University Special Collections, 'Special Collections: DUL MS Cosin V.V.18 Biblia s. Xiii - Durham University', accessed 24 March 2020, https://www.dur.ac.uk/library/asc/theme/medmss/apvv18/.
[7] Robert Branner, *Manuscript Painting in Paris during the Reign of Saint Louis: A Study of Styles*, California Studies in the History of Art 18 (Berkeley: University of California Press, 1977), p. 144, plate 5.

Figure 3: (left) A close up of Plate 5 from Robert Branner's "Manuscript Painting in the time of Saint Louis" and (right) a close up of the initial from fol. 316r.

Palette

Use of Blue

Figure 4: A photograph of Cosin V.v.18 fol. 94v - full page (left), and close up of the initial P (right).

As can be seen in Figure 4, blue is used in the initial of fol. 94v as the ground and the main colour, embellished with white horseshoe-shaped lines. Examination by Raman spectroscopy of a spot in the blue stem of the initial 'P' revealed the pigment to be lapis lazuli, with Raman peaks at 550, 1102 and 1647 cm^{-1}. These are consistent with published library data, which report peaks at 545, 1096 and 1662 cm^{-1}.[8] The exact spot examined, and the spectra obtained can be seen in Figure 5.

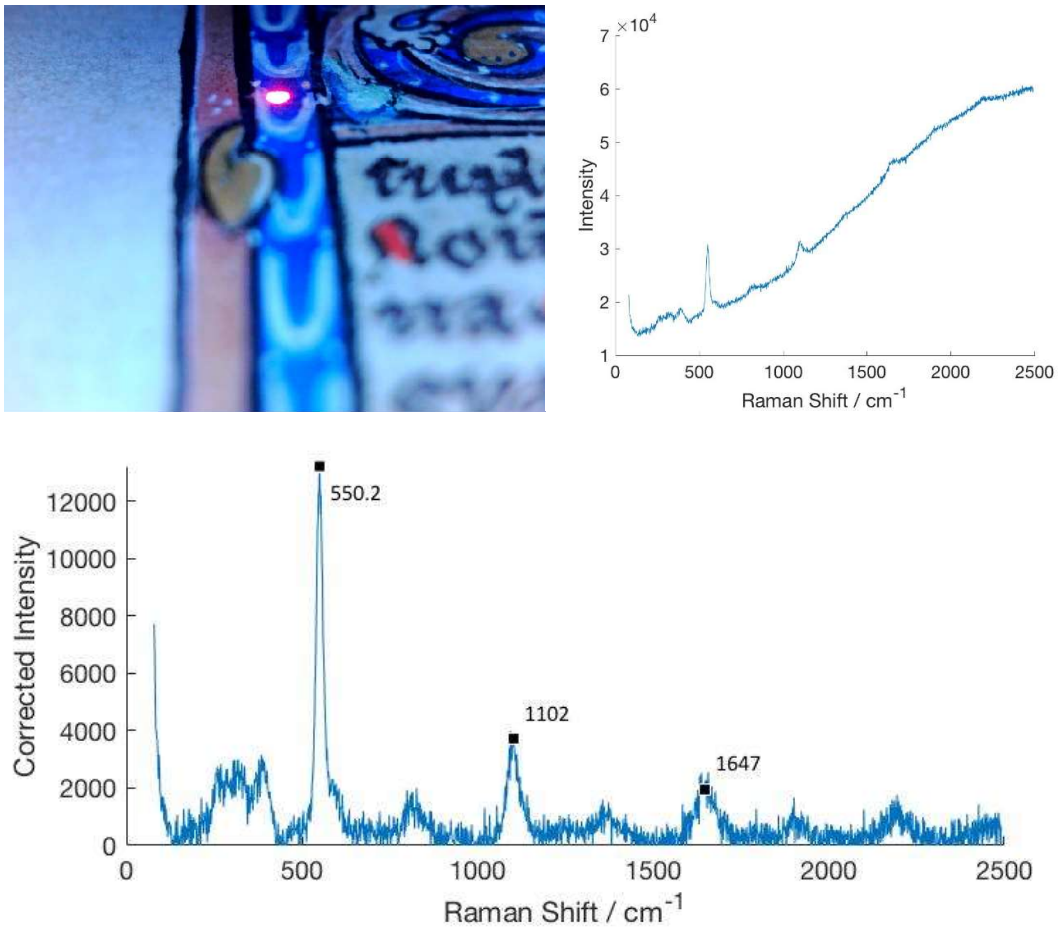

Figure 5: (top left) The spot analysed on Cosin V.v.18 fol. 94v, (top right) the raw spectrum obtained, and (below) the processed spectrum.

When examined by FORS, the blue in the initial was found to contain only lapis lazuli, with no azurite. This is evidenced by the FORS spectrum, as shown in Figure 6, which has an absorbance maximum at 600 nm, consistent with that in published data for lapis lazuli at 600 nm.[9] No azurite absorbance peaks

[8] G. Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', *Analytical Methods* 10, no. 10 (2018), p.1222.
[9] Maurizio Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', *Analytical Methods* 6, no. 5 (2014), p.1491.

were seen between 2000 and 3000 nm, indicating that the lapis lazuli was deployed alone, and was not mixed with azurite.

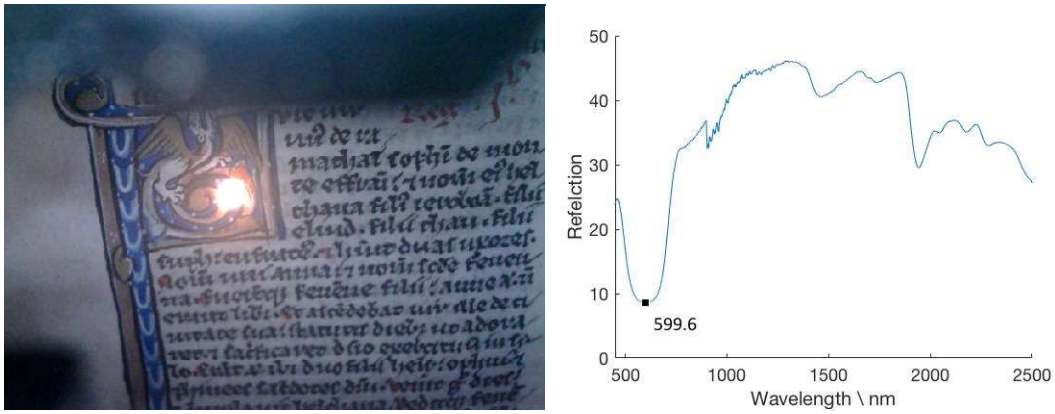

Figure 6: (left) The spot on fol. 94v that indicates where the blue pigment was analysed by FORS, and (right) the resulting FORS spectrum.

A blue pigment is also seen in the initial on fol. 316r, seen in full in Figure 3. Here the blue was used to paint the looping stems. This blue was also found to be lapis lazuli, as shown in Figure 7 below, with Raman peaks at 550, 1096 and 1641 cm^{-1}. These are consistent with published library data, which report peaks at 545, 1096 and 1662 cm^{-1}.[10]

[10] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

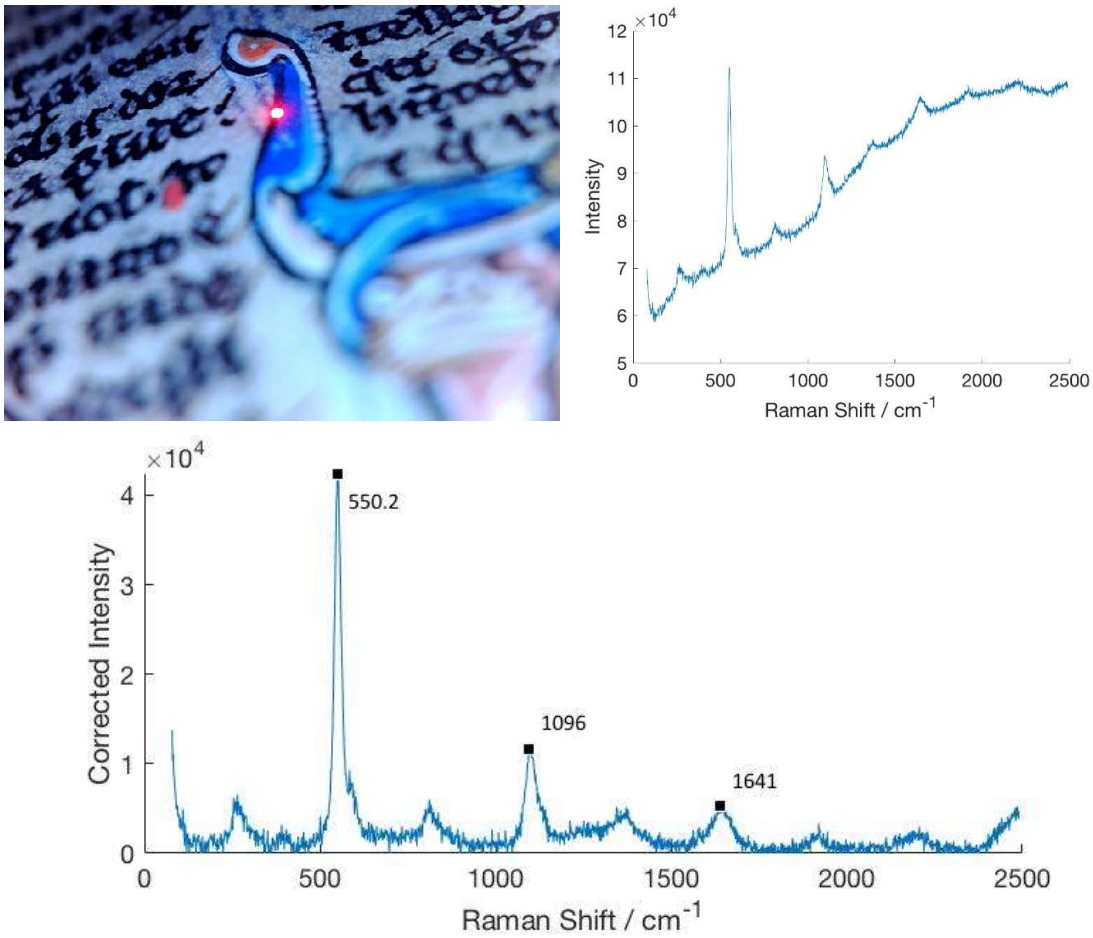

Figure 7: (top left) The spot on fol. 316r where the unprocessed spectrum (top right), and processed spectrum (bottom) were obtained.

However, unlike the previous initial, when examined by FORS the spectrum from one of the blue colours in the decorated initial, shown in Figure 8, revealed that that azurite was deployed as well as lapis lazuli, as there are absorption bands at 2289 and 2354 nm which correspond to those given for azurite in published works.[11]

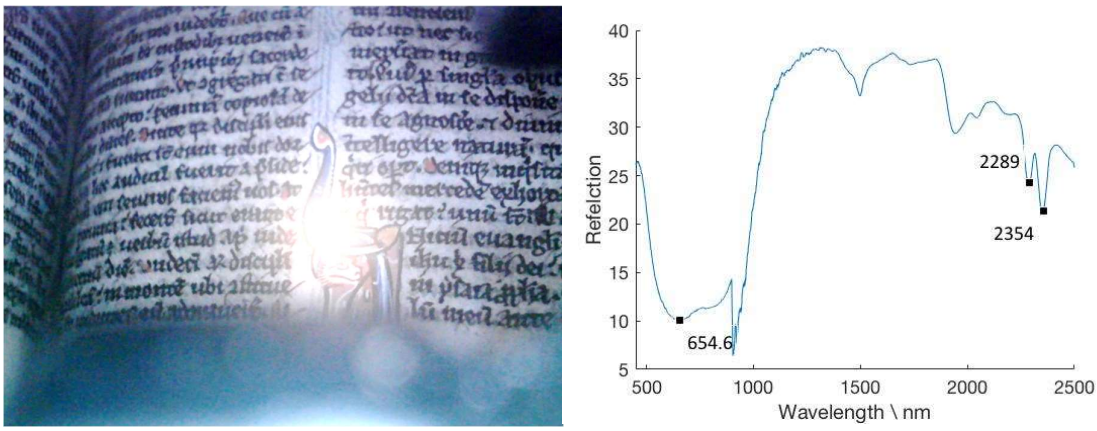

Figure 8: (left) The spot on DUL Cosin V.v.18 fol. 316r, which shows the area where the blue pigment was examined by FORS, and (right) the spectrum obtained.

As seen in Figure 9, photographs taken under white light (400 - 700 nm) and near-infrared illumination (850 nm) depict the areas in the initial where the azurite is deployed in contrast to the lighter lapis lazuli. As explained in chapter two, under the infrared wavelengths, azurite appears dark (seen in the infill behind the creature's head and in the infill behind the curl at the bottom of the initial, for example) whilst the lapis lazuli (in the foliate forms above and below the curl, for example) appears lighter. The two pigments are painted in zones that are close together but are they are not mixed, and never overlap.

[11] R. Mulholland et al., 'Identifying Eighteenth Century Pigments at the Bodleian Library Using in Situ Raman Spectroscopy, XRF and Hyperspectral Imaging', *Heritage Science* 5, no. 1 (18 October 2017), p.11.

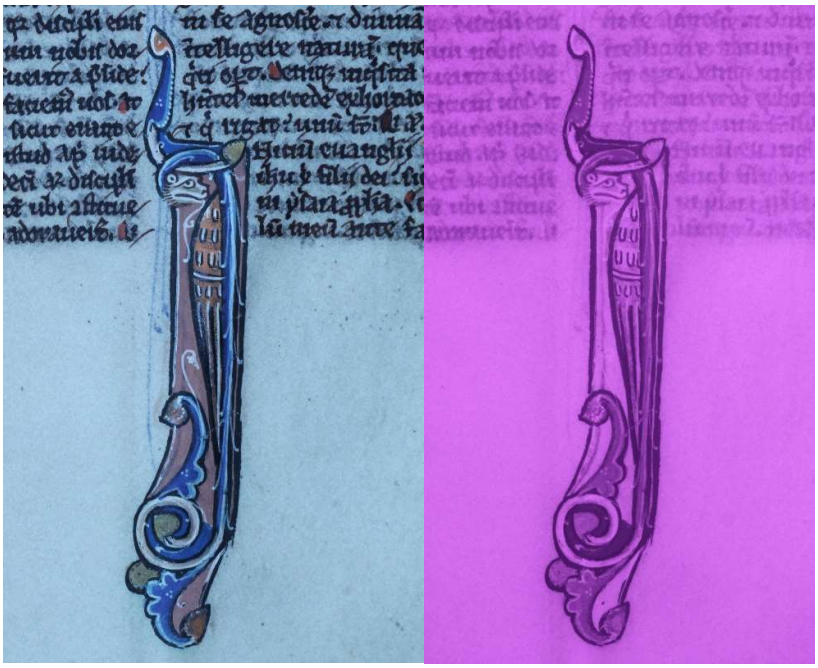

Figure 9: DUL Cosin V.v.18 fol. 316r (left) under white light, and (right) under NIR illumination.

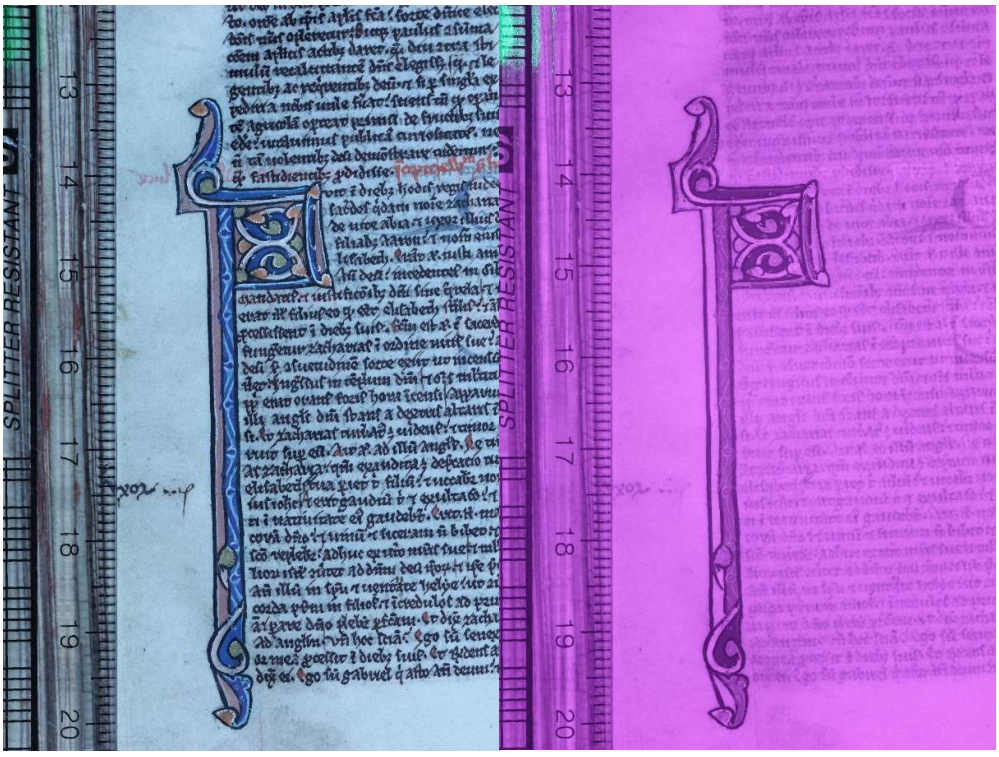

Figure 10: DUL Cosin V.v.18 fol. 323v (left) under white light, and (right) under NIR illumination.

Fol. 323v was also photographed, as seen in Figure 10, and again displayed azurite and lapis lazuli decoration in different zones - close together but never mixed. However, when Fol. 352v was

photographed under white and NIR wavelengths, as seen in Figure 11, the initial 'P' was dark under infrared illumination and was therefore considered to be pure azurite, whilst the text initial at the top of the photograph was light and indicate that lapis lazuli was employed.

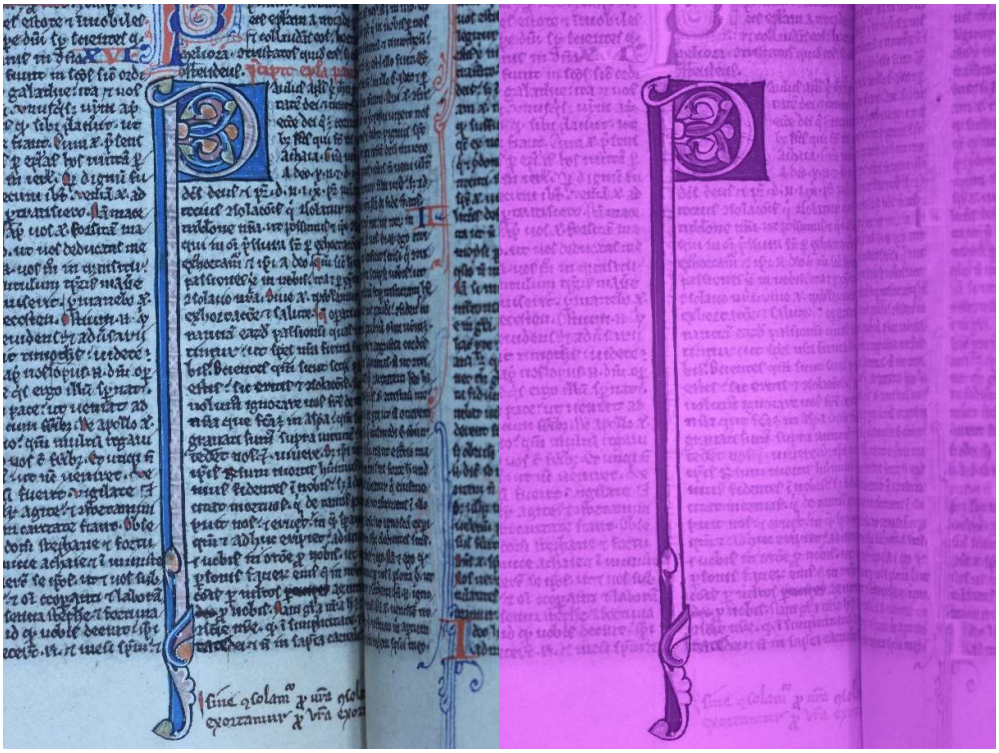

Figure 11: (left) The decorated initial of DUL Cosin V.v.18 fol. 352v under white light, and (right) under NIR illumination.

In the four folios above, then, we see an initial painted with pure lapis lazuli, one with pure azurite, and two with both lapis lazuli and azurite in distinct areas.

Use of white

As described above, white horseshoe shapes decorate the blue initial, and this pigment was found to be white lead. As Figure 12 shows below, the spot examined yielded the spectrum below with peaks at 112 and 1053 cm^{-1}. Published data record white lead peaks at 110 and 1050 cm^{-1}.[12] No processed spectrum has been provided, as in this instance the spectrum foregrounds the signal from the lapis lazuli, which is also present here, as the white lead is sitting on top of lapis lazuli.

[12] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

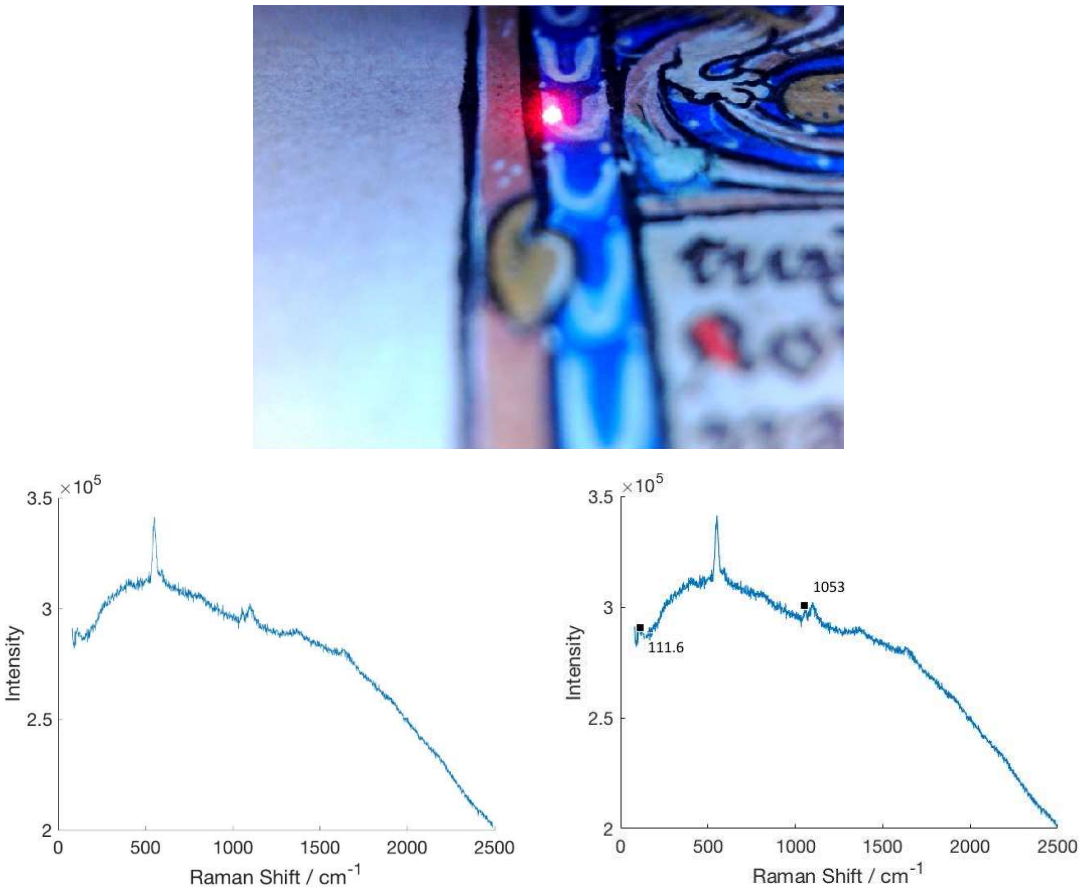

Figure 12: Cosin V.v.18 fol. 94v (top) the point where Raman spectrum of white pigment taken, (bottom left) the raw spectrum, and (right) the labelled raw spectrum.

The white on the leg of the creature on fol. 94v was examined by FORS and found to be white lead, as shown in Figure 13 by the band at 1447 nm which is consistent with published data for white lead (at 1447 nm).[13]

[13] John K. Delaney et al., 'Use of Imaging Spectroscopy, Fiber Optic Reflectance Spectroscopy, and X-Ray Fluorescence to Map and Identify Pigments in Illuminated Manuscripts', *Studies in Conservation* 59, no. 2 (March 2014), p. 97.

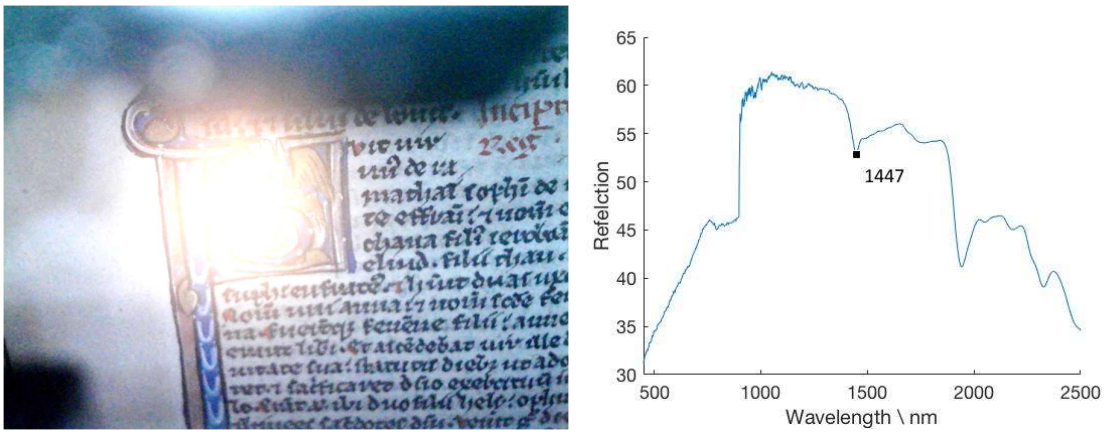

Figure 13: (left) The spot on DUL Cosin V.v.18 fol. 94v examined by FORS, and (right) the spectrum recorded.

Use of orange

As seen in Figure 4 above, an orange colour is used, sparingly, to decorate the bottom of the extender of the initial 'P' on fol. 94v. This was found to be red lead, as demonstrated in Figure 14 below. The Raman peaks at 122 and 550 cm^{-1} correspond to published data for red lead, which give the peaks at 121 and 549 cm^{-1}.[14]

Another peak is present in the spectrum obtained for red lead at 363 cm^{-1}, although this may be an artefact of the processing, as they are not visible in the raw spectrum. Massicot is often a contaminant of red lead, but its peaks (at 70, 86, 142, 215, 384 and 423 cm^{-1} with 142 cm^{-1} being the strongest) do not correspond to any of the peaks in the processed spectrum.[15]

[14] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.
[15] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

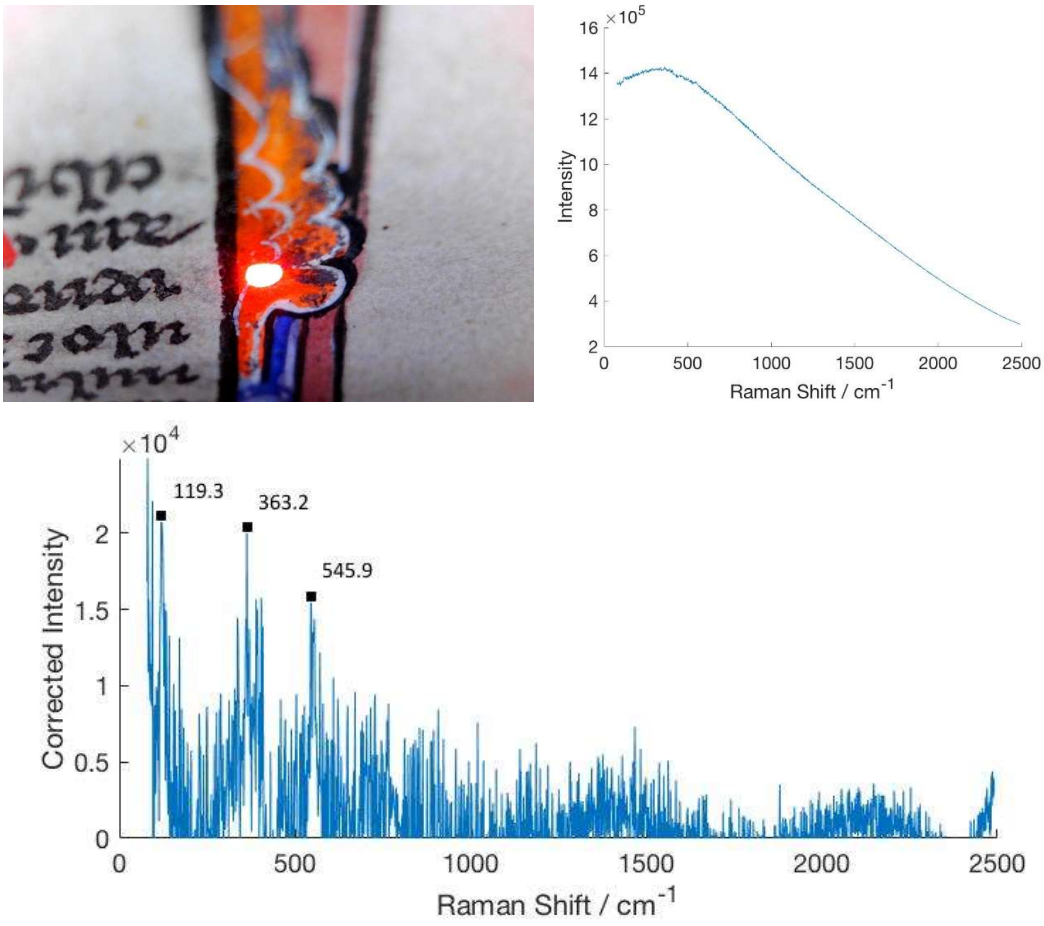

Figure 14: (top left) The spot on the orange colour on fol. 94v where the raw spectrum (right), and processed spectrum (bottom) were obtained.

When examined by FORS, the spectrum of the red at the bottom of the initial was confirmed as red lead, with an inflection point at 563 nm (Figure 15), which is consistent with that given for red lead in published data (at 565 nm).[16]

[16] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

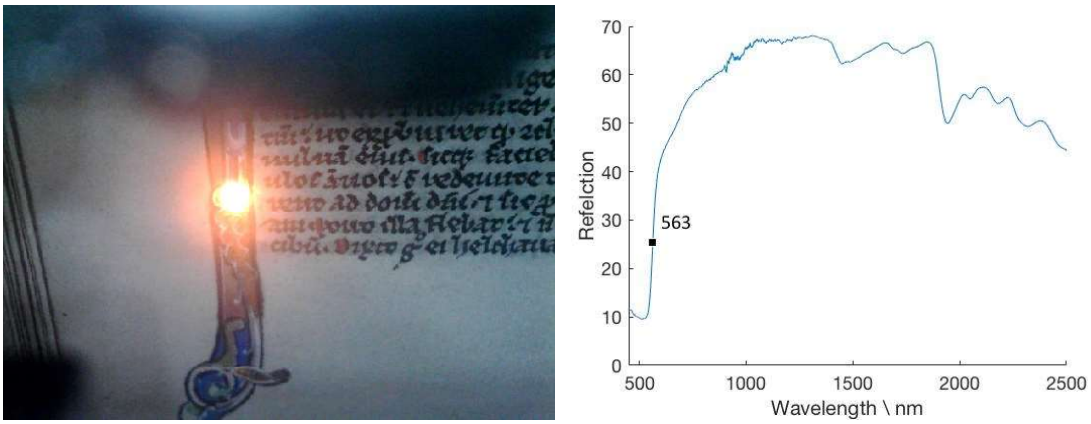

Figure 15: (left) The spot on DUL Cosin V.v.18 fol. 94v where the FORS spectrum was taken, and (right) the spectrum obtained.

Use of yellow

As mentioned above, the manuscript contains a yellow-brown colour that could be mistaken for a dull gold. In some manuscripts, pigments such as mosaic gold and orpiment have been used in an attempt to replicate, and sometimes even possibly to fabricate gold. However, despite its golden appearance, the fact that there is detail added over the colour, as can be seen in the close-up in Figure 16 below, suggests that this is not an attempt to deceive. Decoration on top of gold is relatively uncommon, although not unheard of, and in addition, gold tends not to be used as a colour in amongst other colours, but as a standout initial or ground. It would be uncommon to see gold used in such small quantities as part of the wider decorative scheme, especially in a book that does not seem to be of the highest grade, adding weight to the theory that the colour was not deployed as a deceit.

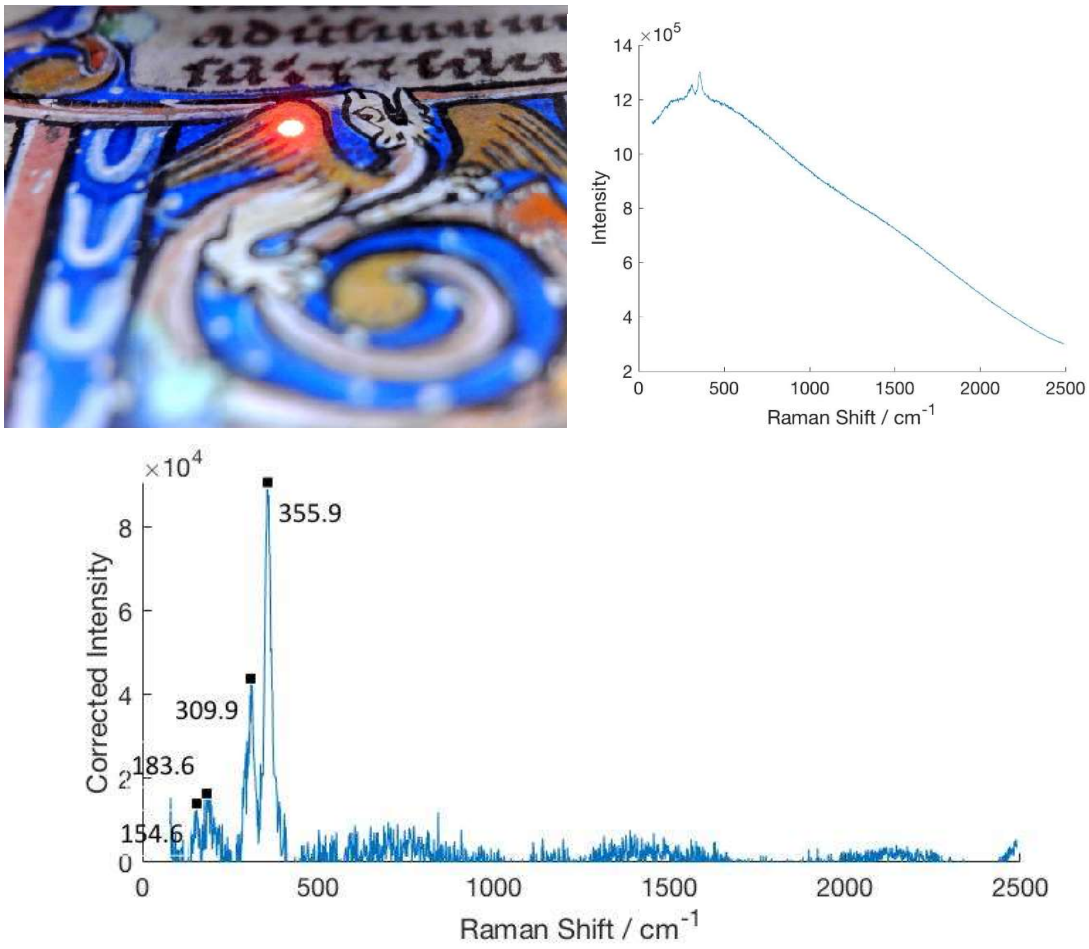

Figure 16: (top left) The spot on Cosin V.v.18 fol. 94v which was examined, (top right) the unprocessed spectrum obtained and (below) the processed spectrum.

When examined, the yellow-brown colour on fol. 94r, shown in Figure 16, returned a spectrum with peaks at 155, 184, 310 and 356 cm^{-1}. This corresponds with published data for orpiment (arsenic (III) sulfide, AS_2S_3), which records peaks at 153, 180, and 309, and 354 cm^{-1}.

A second example of the yellow-brown colour was examined on a different fol., fol. 316, as shown [17]in Figure 17, below. Again, the spectrum returned similar peaks to that seen in Figure 16 at 158, 197, 313 and 358 cm^{-1}, which correspond with those given for orpiment.[18]

[17] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p.1222.
[18] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

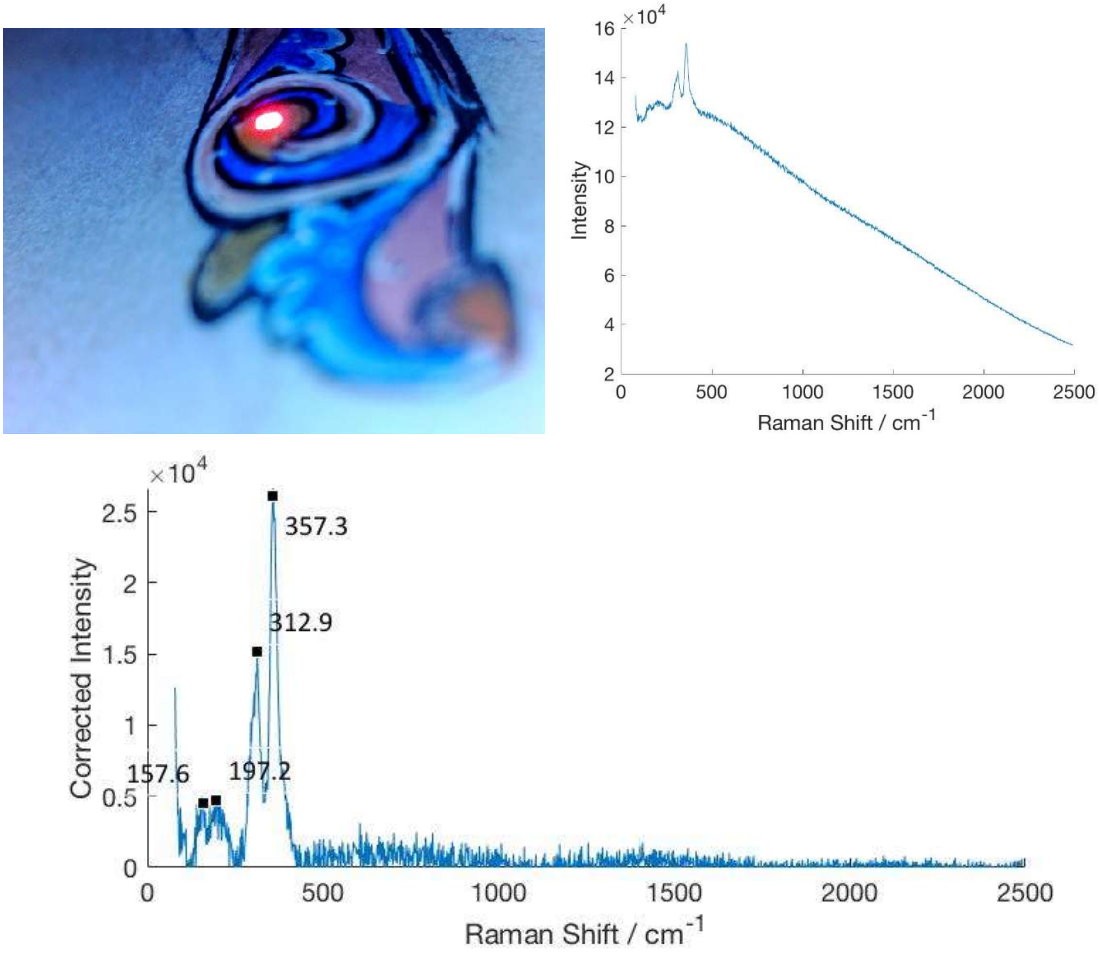

Figure 17:(top left) The spot on the decoration on fol. 316r where the raw Raman spectrum (top right) and the processed spectrum (bottom) were obtained.

It is prudent to mention here that realgar (arsenic sulfide (As_4S_4)) is a related pigment to orpiment and has more of a brown-yellow colour than orpiment, which is usually bright yellow. However, the use of realgar here is discounted, as although its Raman spectrum is similar, with the most intense peak at 354 cm^{-1} and another peak at 191 cm^{-1}, it does not have a peak at 157 or 309 cm^{-1} unlike those found in the areas examined.[19]

Use of green

If orange is employed sparingly in the decoration of the manuscript, then the deployment of green is positively meagre, as can be confirmed by the tiny amounts seen in Figure 1 above and Figure 18 below. In fact, in Figure 18, the area of green examined is so small that the laser spot covers it entirely.

[19] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

Nevertheless, a Raman spectrum of sorts was obtained, which shows that the pigment absorbs the laser energy, and is therefore likely to be copper-based. The peaks seen below 500 cm^{-1} are in fact an artefact of the Raman system that is only seen when the Raman signal is very weak, i.e., when the laser beam is being absorbed.

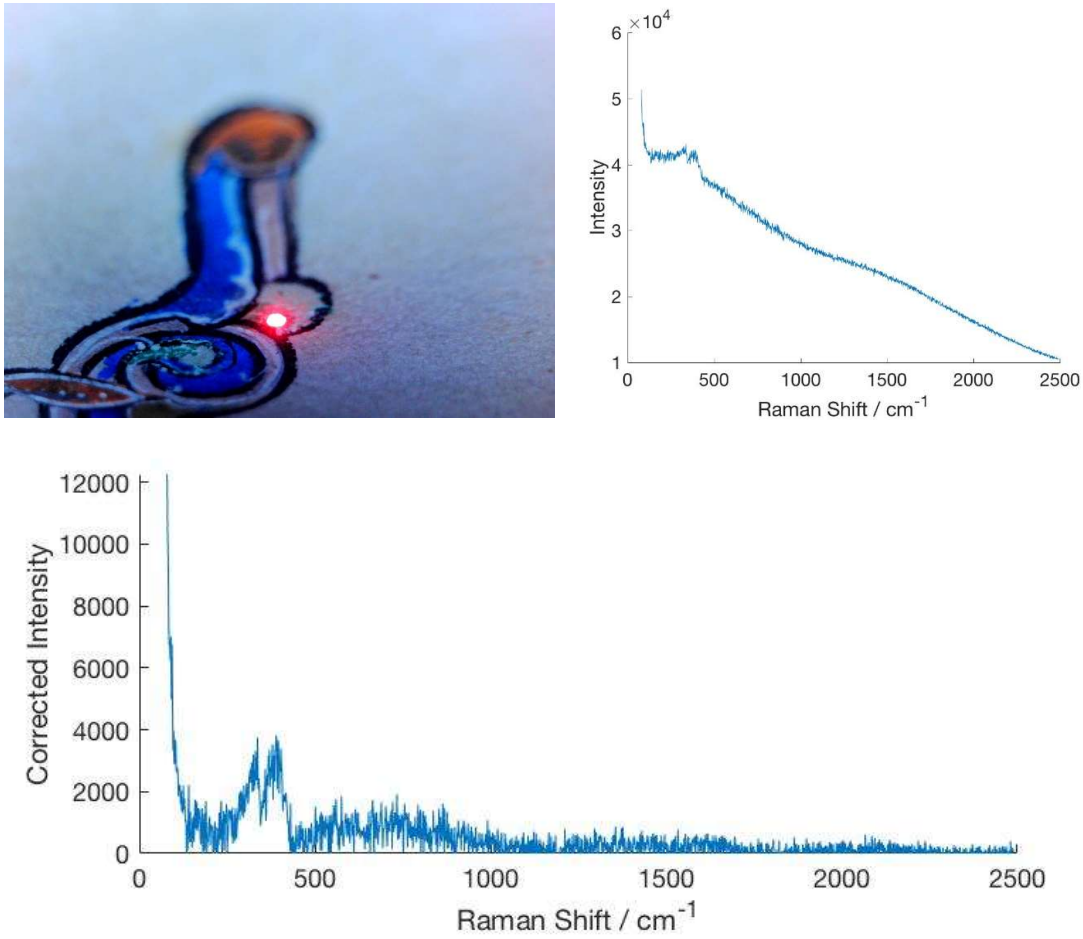

Figure 18: Cosin V.v.18 fol. 94v, showing (top left) the green spot examined, (top right) the spectrum obtained, and (below) the processed spectrum.

As discussed in chapter two, the most common copper-based pigment used in manuscripts is verdigris, and it is highly likely that this is what the pigment is. Malachite, which is also copper-based, gives a Raman spectrum with peaks at 162 and 188 cm^{-1}, as potentially seen in the green in Cosin V.v.17, so its use here can be discounted. Furthermore, the colour of the pigment is quite vibrant which would be difficult to obtain from organic greens such as sap green and iris juice, and these would likely fluoresce under the Raman laser and so can also be discounted. Green earth is one possibility for this pigment that cannot be ruled out, although its presence would be unusual, as verdigris is used in many comparable manuscripts, being stable and easy to manufacture.

Use of Brown

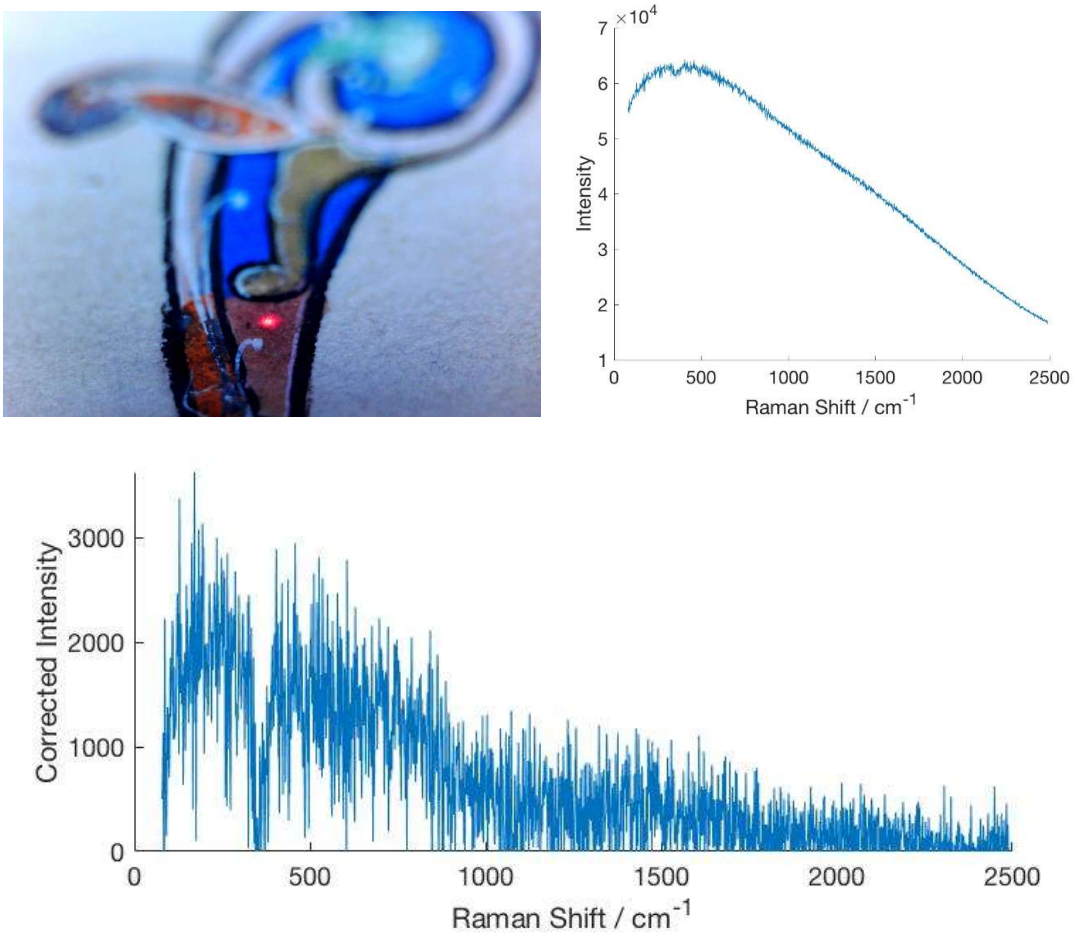

Figure 19: Cosin V.v.18 fol. 94v showing (top left) the exact spot where the Raman signal was obtained, (top right) the unprocessed spectrum, and (bottom) the processed spectrum.

As can be seen in Figure 1 and Figure 19 above, there is a small patch of brown colourant at the bottom of the descender of the letter 'P'. After examination with the Raman system, the raw and processed spectra did not yield any peaks to aid identification of this colourstuff, although the raw spectrum does show that the colourant fluoresces slightly. Browns are often a concoction of other colourants, including organic components, which yield no Raman spectrum bar fluorescence that we do see here, and so it may be that the colourant is a mixture containing some or all organic constituents. Brown or red ochre, which the substance may also be, can yield a Raman signal but it can be difficult to obtain, so it too, remains a possibility for the identification of this colourant. A FORS spectrum could potentially give more information, but was unobtainable due to the small size of the patch of colour.

The 'blip' at about 400 cm^{-1} is caused by an error in the setup of the Raman system (and can also be seen in Figure 20).

Use of pink

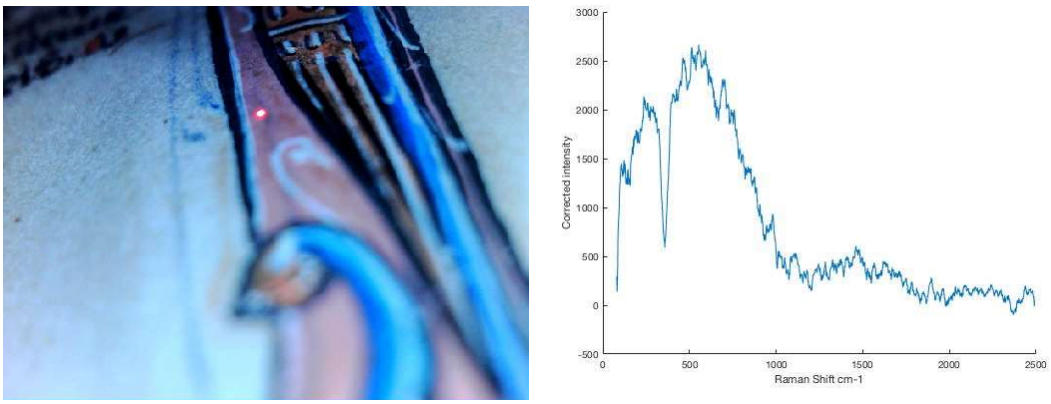

Figure 20: (left) The spot on fol. 316r examined, and (right) the processed spectrum obtained.

Like the brown described above, the pink colour, shown in Figure 20 above, returns no discernible Raman spectrum, bar fluorescence, indicating a likely organic component. A FORS spectrum here may have provided some clarity.

Use of black

Black, as mentioned above, is used to outline the infills in the initials, providing neat edges to the paints already applied. Although it can sometimes be difficult to acquire spectra from such thin lines, on this occasion, a spectrum showing that the black line was carbon (lamp black) was obtained, as shown in Figure 21. Here the carbon peaks at 1337 and 1611 cm^{-1} are clearly shown.[20]

[20] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

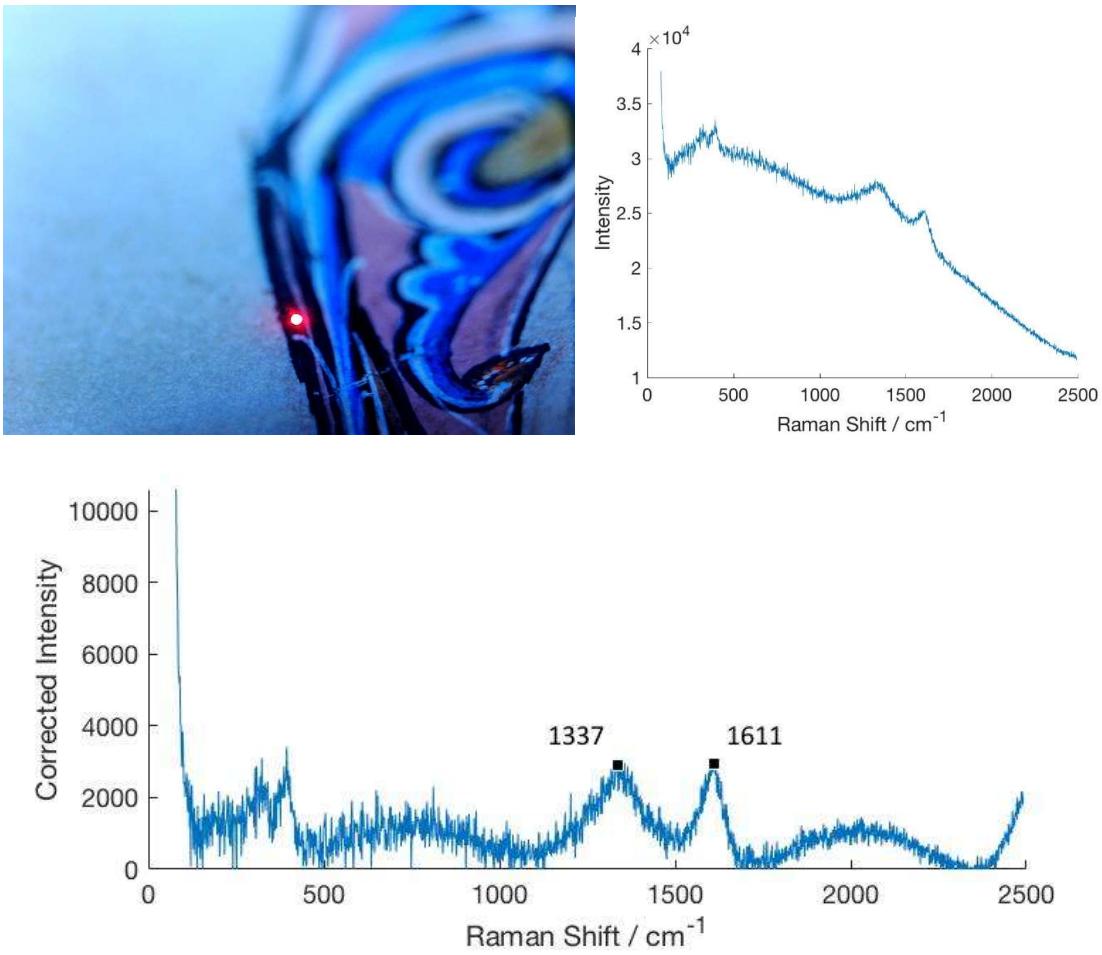

Figure 21: (top left) The spot on fol. 316r examined with Raman spectroscopy, (top right) the raw spectrum obtained, and (below) the processed spectrum.

Text ornamentation

Running Headings

As described above, running headings in alternate blue and red capital letters, denoting the book names, were used as a signifier across each opening. The red letters were painted in vermilion, as is evidenced in Figure 22. The Raman peaks at 251 and 344 cm^{-1} are consistent with published data, which report the peaks at 258 and 341 cm^{-1}.[21] The peak at 342 cm^{-1} is not visible in the unprocessed spectrum and is barely visible in the processed spectrum, which is unusual as vermilion usually provides a very strong Raman signal (compare with Figure 26 below). It may be that the binder used

[21] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p.1222.

to make the vermilion pigment into paint is fluorescing under the Raman laser, and masking the signal of the peak.

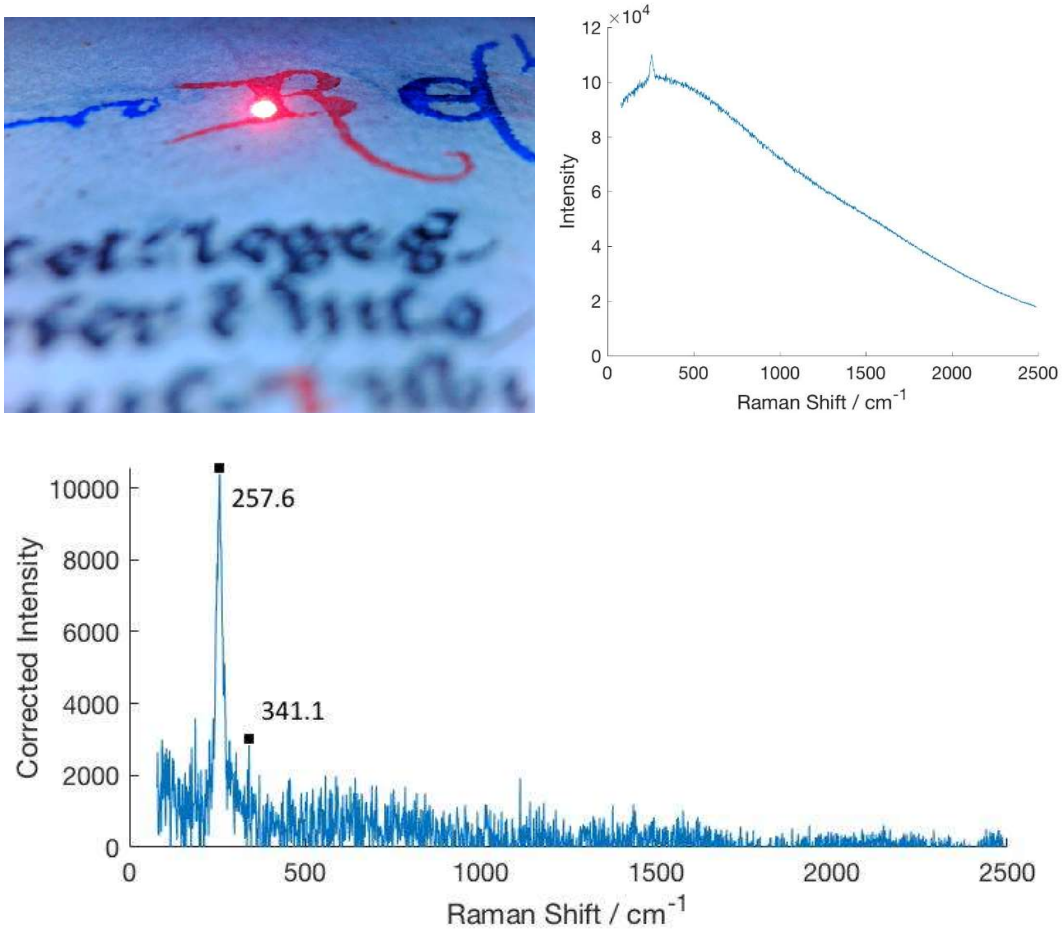

Figure 22: (top left) The spot on the running heading on Cosin V.v.18 fol. 94r where the Raman signal was obtained (top right) the raw spectrum and (below) the processed spectrum.

Figure 23 shows the results obtained when a blue capital in the running heading was examined. As can be seen from the spectra, the pigment is lapis lazuli.

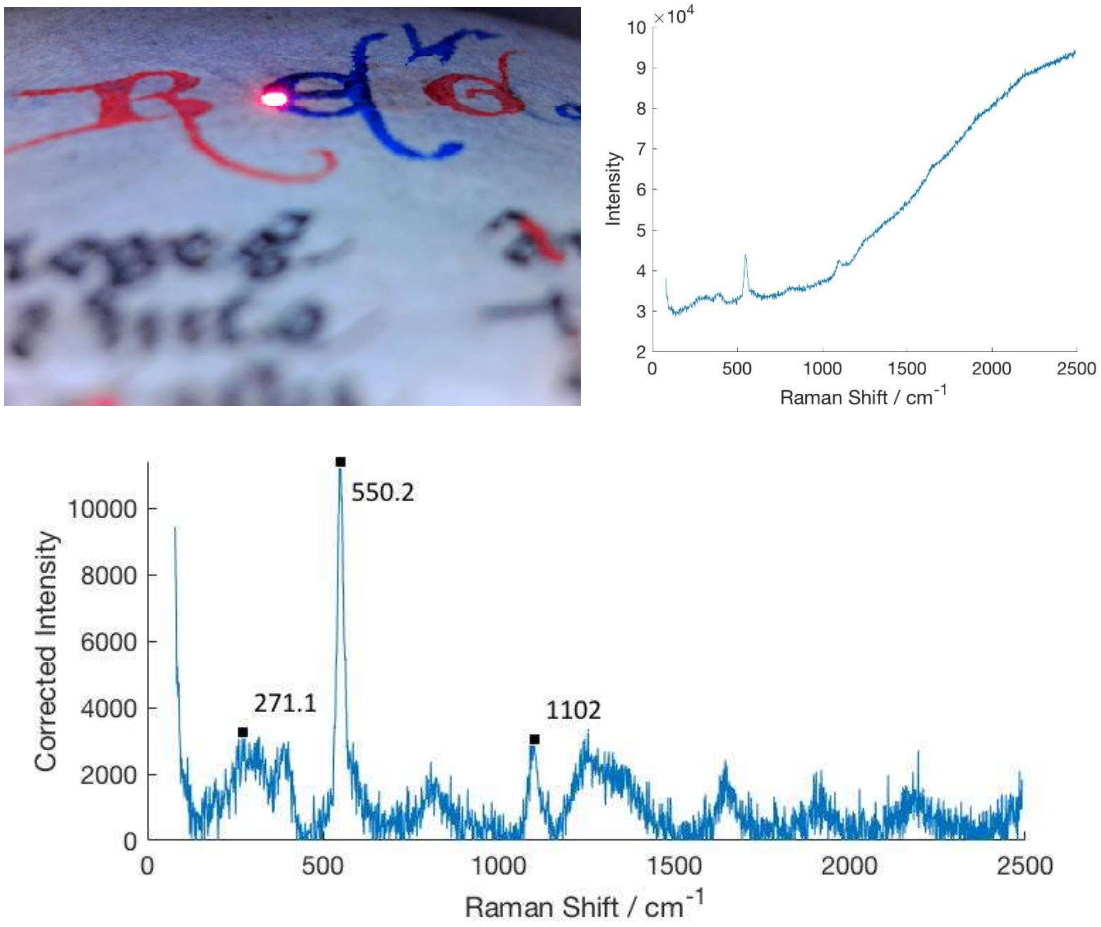

Figure 23: (left) the spot on the running heading on Cosin V.v.18 fol. 94r where the Raman signal was obtained (centre) the raw spectrum and (right) the processed spectrum.

The FORS spectra from fol. 94v also confirm that the running headings are vermilion and lapis lazuli, featuring an inflection point at 600 nm consistent with the former (Figure 24) and an absorbance maximum of 600 nm indicative of the latter (Figure 25).[22] These FORS spectra confirm the data obtained from the Raman spectrometer.

[22] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry' p. 1491.

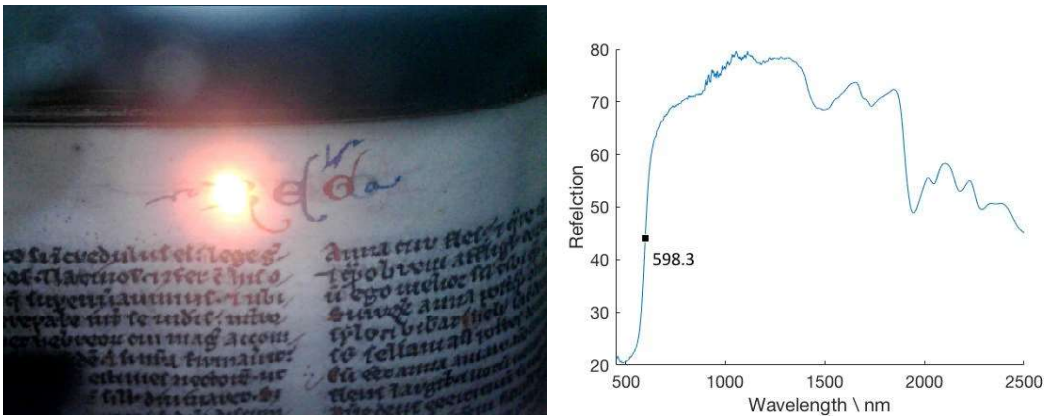

Figure 24: (left) The spot in the running heading on DUL Cosin V.v.18 fol. 94v where the FORS spectrum was taken, and (right0 the spectrum obtained.

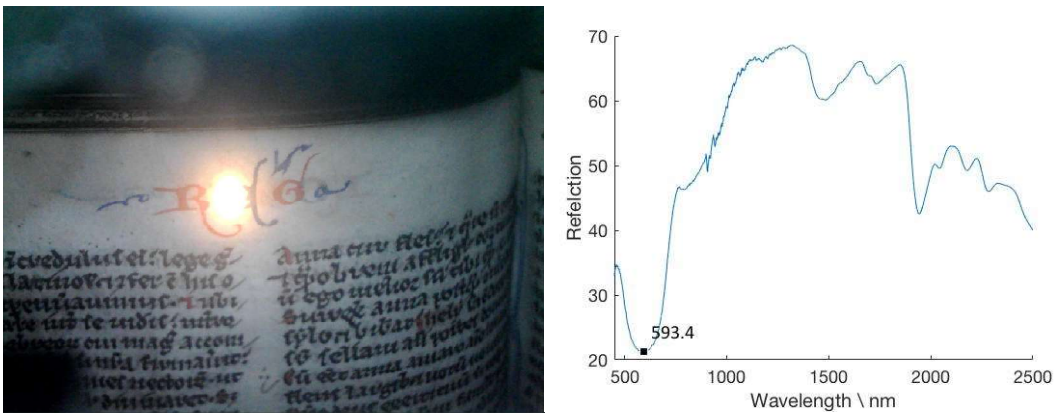

Figure 25: (left) The spot in the running heading on DUL Cosin V.v.18 fol. 94v where the FROS spectrum was taken, and (right0 the spectrum obtained.

The deployment of lapis lazuli for the blue in the running headings is notable given that azurite, a cheaper blue and one that was evidently available (as seen above), was used for more formulaic artwork and text ornamentation. This probably reflects the subdivision of labour and/or materials in the atelier.

Rubric

Figure 26 below shows that the rubric examined on fol. 94r is vermilion. The vermilion signal is much stronger than that obtained for the running heading, as seen in Figure 22 above, possibly due to the nature of the binder. The Raman peaks at 256 and 349 cm^{-1} are consistent with the published Raman data that records the peaks at 251 and 342 cm^{-1}.[23]

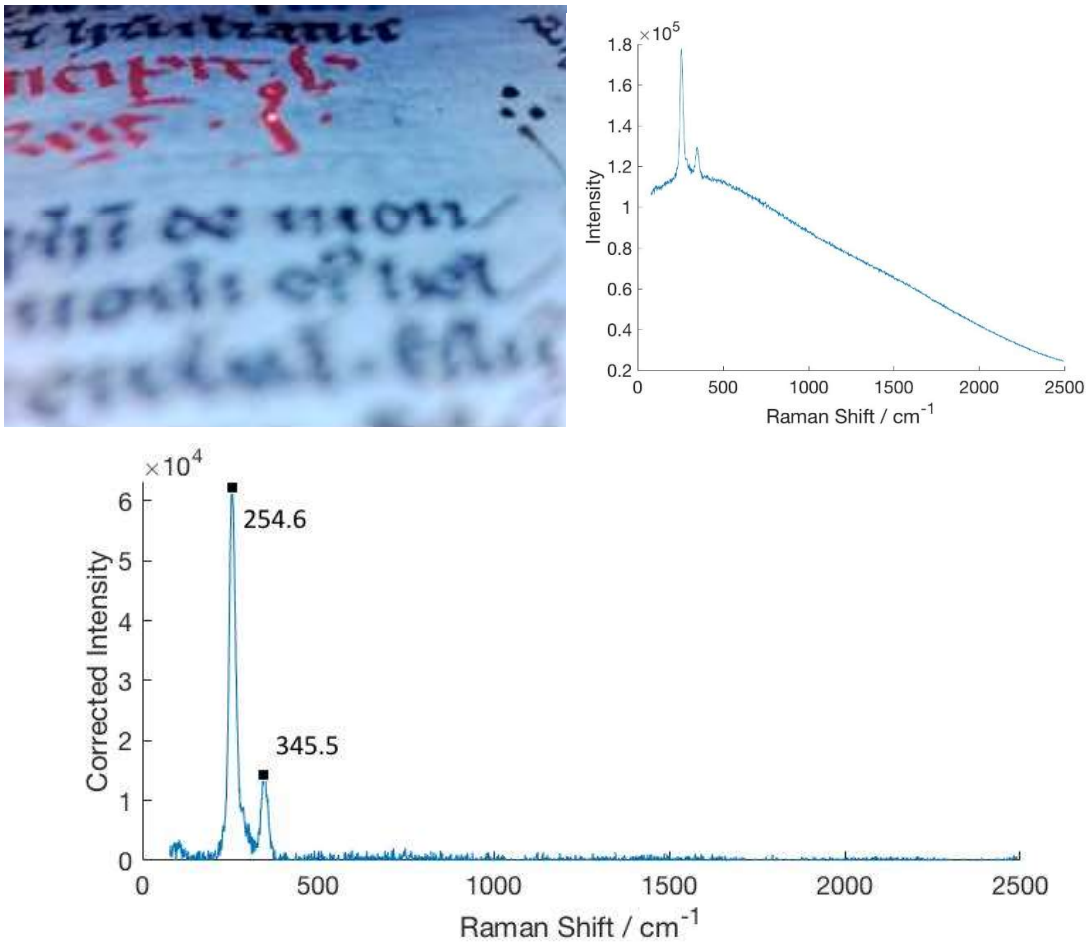

Figure 26: (top left) The spot on the rubric where the on Cosin V.v.18 fol. 94r where the Raman signal was obtained, (top right) the raw spectrum, and (bottom) the processed spectrum.

[23] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p.1222.

Ink

The ink used to write the small, neat Gothic Textura, as seen in Figure 2 above and Figure 27 below, is very black. Oak gall ink, the standard ink used for texts in manuscripts of this period, sometimes had carbon as an additional constituent, in order to make the ink blacker. However, as Figure 27 and Figure 28 demonstrate below, when examined by Raman the ink on fol. 94 and 326r does not appear to contain any carbon.

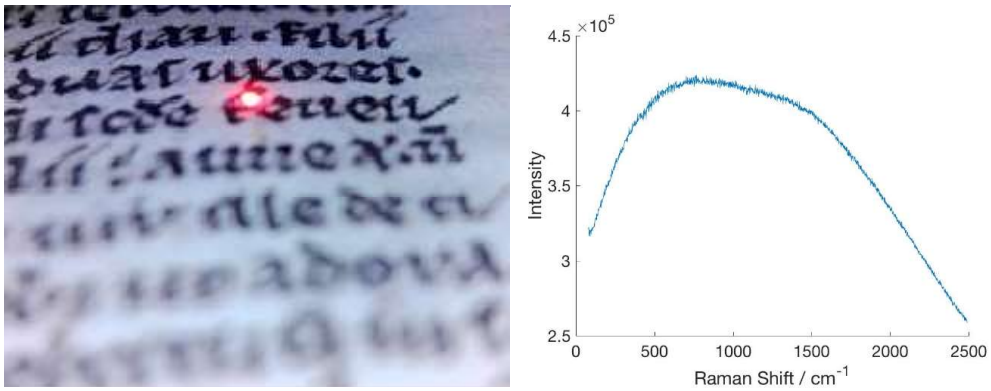

Figure 27 (left) The spot on the black ink where the on Cosin V.v.18 fol. 94r where the Raman signal was obtained, and (right) the raw spectrum obtained.

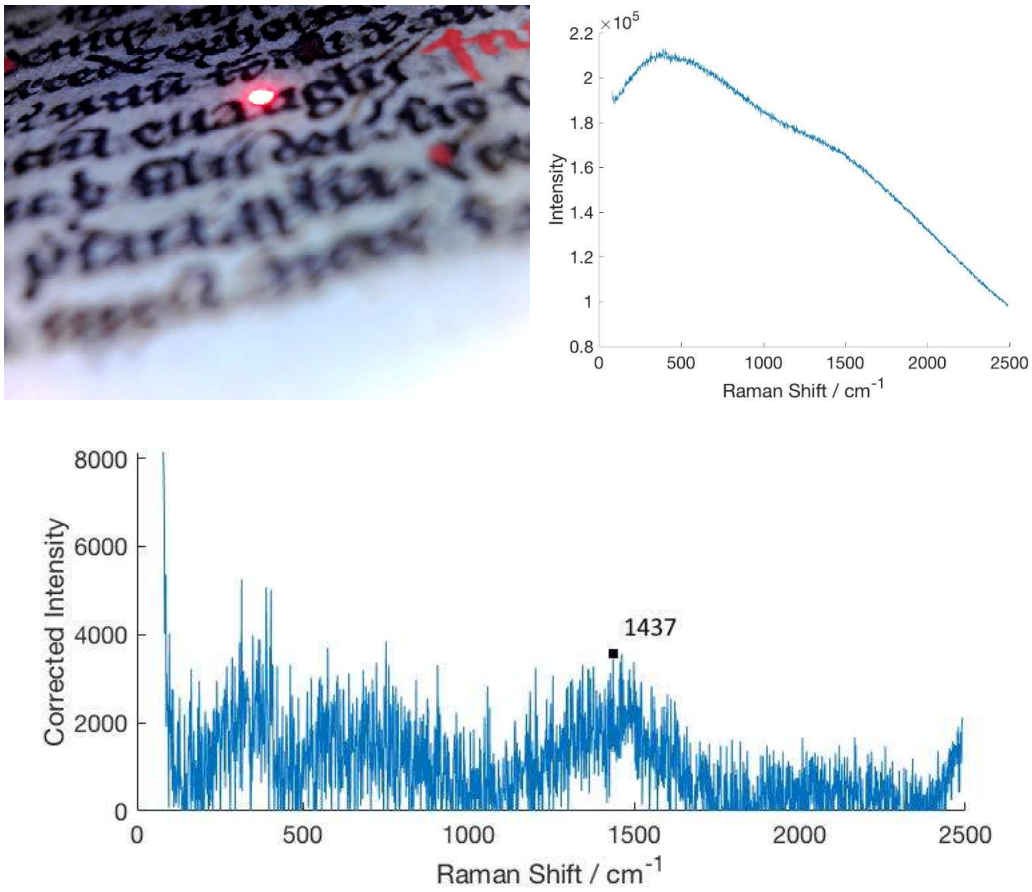

Figure 28: (left) The spot on fol. 316r where the ink was examined and (right) the Raman spectrum obtained.

Further comments on the palette as a whole

The pigments definitively found from the folios examined in Cosin V.v.18 were lapis lazuli, azurite, red lead, white lead, carbon, orpiment and vermilion. It is likely that iron gall ink was used, as well as a copper green, an organic-based pink and an organic-based brown.

With the exception of orpiment, all of the pigments used are typical of those seen in the thirteenth century, and indeed those seen in the thirteenth-century French bibles so far examined. It is not unknown to see orpiment in a manuscript of this time, but it is a period in which orpiment is not commonly seen. It is unusual not to see gold, but this is likely an economic choice, and there are hints in the book's codicology that this manuscript was not of the highest grade.

The colouration of the blue initials is interesting. Sometimes lapis lazuli alone was used, sometimes only azurite, and at other times both were deployed to colour the same initial, although they were never mixed. The seemingly random choices of blue pigment used in this way suggest that the

pigments applied were an artistic choice, with the different tones of blue that lapis lazuli and azurite have combining to produce the overall effect.

Durham Cathedral Library A.IV.30

Note

Two folios from Durham Cathedral Library A.IV.30 were examined at Durham University Library with the Raman spectroscopy system, the FORS system and the microscopy system in February 2020. On account of the closure of the library due to the Coronavirus outbreak, there was no opportunity to examine further folios or to redo spectra that seemed erroneous or interesting. In particular, the spectra from the FORS system are not of high quality, and the photomicrographs from the FORS system are particularly dark, so examination with the FORS system would have been redone. In addition, there was no opportunity to perform any multispectral imaging or a codicological examination of the book with the chance to photograph other folios.

Description and provenance

The manuscript known as DCL A.IV.30 is another thirteenth-century French Bible in the Durham Cathedral Library collection and is dated to the second half of the century. The book contains a list of Biblical books and canticles, followed by a calendar (with relatively few feasts indicated) and a lection schedule. There is then the Bible in the usual 'Paris Bible' order with the common set of prologues (with a few exceptions) followed by the list of Hebrew names, as is usual.

Figure 29: Durham University Library A.IV.30, fol. 15v and 16r.

At present, the manuscript is not part of the Cathedral's Online Priory collection, as it has not yet been digitised. A catalogue of Durham Cathedral's manuscripts is currently being compiled, but as yet this manuscript's entry is not online, so details are taken from a draft copy.[24]

As can be seen from Figure 29 above, the book is of diminutive size, measuring 160 x 105 mm, and is thus categorised as pocket-sized. It has 572 folios, bookended by modern flyleaves, and a medieval flyleaf at the start. Its wooden binding dates from 1846, but possibly reuses older wooden boards. The book has been in the Durham collection since 1729 when it was received from Henry Bland, then Dean of Durham.

Previous owners include a possible Richard Winwood in the seventeenth century, Witham Charterhouse in the fifteenth/sixteenth century and William Loryng (d. 1415/6) who was, at various times, Canon of Bangor, Lincoln, Wimborne, and Salisbury.

Fortuitously, the book gives some indication as to its date of creation with the inclusion, as an original entry in the calendar, of the canonisation of Peter of Verona in March 1253, which shows that the book was made after this date. The dedications of the friary and cathedral of Besançon in Eastern France give an indication of its intended recipients - as well as the cathedral and friary at Besançon being Dominican, there are also several calendar dates that indicate a Dominican interest. Robert Branner has classified A.IV.30 as being a manuscript from the Mathurin Atelier (discussed in detail below), which was a workshop in the university district of Paris that specialised in Vulgate Bibles.[25]

Codicology

Quire formation

Most of the book is in collations of 18 or 20 leaves, with one quire of 8, one of 6 and one 2.

Parchment and ruling

Like Cosin V.v.17 and Cosin V.v.18, A.IV.30 has wafer-thin parchment that is fine and even-toned, apart from two folios at the start. The parchment is so thin that the hair and flesh sides are indistinguishable. Most of the pricking has been excised, but occasionally some awl pricking remains in the lower margins. The ruling was done in lead.

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[24] Richard Gameson, *The Medieval Manuscripts of Durham Cathedral: A Descriptive Catalogue (in Progress)*, 2020.
[25] Branner, *Manuscript Painting in Paris during the Reign of Saint Louis*, p.3.

Despoliation

There is some staining on fols. 518 to 522 and two strips cut from the lower margin of fols. 550 and 569 (which is a bifolium, suggesting this strip was cut at the manufacturing stage). The corner of fol. 463 is torn and one corner, on fol. 528 is cropped, probably to prevent further damage from a former tear.

Text layout, ornamentation and rubrics

As can be seen in Figure 29 and Figure 30, the manuscript has black text that is arranged in two columns per page, each of 47 lines. The text block measures 74 x 106-110 mm, with each column measuring 34 mm across.

Figure 29 also shows the running headings that are seen across an opening, in alternating blue and red capitals.

Figure 30: A close-up image of the top half of DCL A.IV.30 fol. 16r.

Text initials, alternately red, then blue, are two lines high, as seen in Figure 30. The text initials are accompanied by alternating red and blue waterfalls cascading down the side of the column. Some words are highlighted in red, and corrections are made in the margin and flourished. In the top left corner, a long blue waterfall signifies the red and blue chapter numbers that are buried within the text.

Figure 31 shows the first page of the Bible proper - Jerome's preface - and also shows several other features of the design of this manuscript. There is a red-orange rubric in an interesting corner layout,

a blue text initial (again, two lines high) with blue and red waterfalls emanating from it, alternate colour flourishing around the text initial and at the bottom of the page, and not forgetting the historiated initial, 11 lines high, at the very beginning of the page. Again, there are 47 lines of text in two columns.

Figure 31: DCL A.IV.30 fol. 12r.

Script and hands

The script is Textualis semi-quadrata, written very compactly, as shown in Figure 30. As expected, the script is very small, in order to accommodate 47 lines per page, and allow the book to be its diminutive size. It seems as if there is only one scribe responsible for the text, and most corrections are by this same hand, probably at the time of writing, whilst a few are in another hand, likely during a later phase of work.[26]

[26] Gameson, *The Medieval Manuscripts of Durham Cathedral: A Descriptive Catalogue (in Progress)*.

Artwork

Style of artwork

Figure 32: (left) The historiated initial on A.IV.30 fol. 15v in full, and (right) close up.

The historiated initials for the general preface and for each biblical book, generally over 10 lines high, are enhanced with border decorations containing foliate loops and beast heads. Where figures are present, they are simplistic but effective, as shown in Figure 33 below, with a few deft lines articulating faces, hair and large noses. Robert Branner characterises the artwork from The Mathurin Atelier with an initial from Psalm 1 of the Mathurin Breviary, as seen in Figure 5. The style of the figures in that initial are very comparable to the style of the figures painted in A.IV.30 - both have simple silhouettes and uncomplicated drapery, are encased in black lines, and have simple facial features with large noses.

Figure 33: (left) The initial from Psalm 1 of the Mathurin Breviary[27] and (right) a close up of A.IV.30 fol. 15r.

Approach to painting

Shown in full in Figure 34 below, the historiated initial on fol. 15v spans the page and contains eight scenes, seven showing God's creation of the world, followed by the crucifixion. Each scene is little over 1 cm high.

Figure 34: A.IV.30 fol. 15r in full.

[27] Image from plate 63 page 144 in Branner, *Manuscript Painting in Paris during the Reign of Saint Louis*.

A close-up image of one of the circles within the initial, shown in Figure 35, reveals much interesting information about painting technique. Here the brief but confident lines that articulate the facial features can be seen clearly, and the thinness of these lines, drawn either with a pen or with a brush with a single hair perhaps, contrasts with the much thicker lines used to outline the drapery, the circle and gold in the initial. Although fairly uncomplicated, it is possible to see how different shades of blue have been used simply but effectively to accentuate the clothing.

Figure 35: (left) A photomicrograph of a section of the initial on DUL A.II 37 fol. 15v viewed under white light, and (right) under infrared.

It is possible to see some lines 'underneath' the top layer of paint, particularly in the arms, when looking at the infrared image. These lines could either be a preliminary drawing sketched by the artist for another painter, or by the painter themselves, which have then been over-painted rather freely to create the final version. Alternatively, the lines could be an attempt to add detail to the clothes, although it is a pretty unsuccessful one if that is the case.

Figure 36: A photomicrograph of the historiated initial on DUL A.II.37, fol. 12r.

In Figure 36 above, the confident and well-placed lines that sculpt the hair and face are shown very clearly, but contrast with the sketchier, overlapping lines used to draw the hands, parchment, pen and knife. Whilst it is not impossible that these were two different artists, it is unlikely. The application of gold in the halo is lacking, and the blue cowl around Jerome's neck seems to have escaped its black line border. Whilst not major, these imperfections give the impression that not every effort was made to make this initial as perfect as it could have been. More attention to detail might have been expected given that this is the first decorated initial in the book. Economy, time-pressures, or a lack of skill may have been factors contributing to this.

Palette

Overview

The palette of the artwork on the folios examined, which is representative of all the folios in the book, consists mainly of a vibrant blue, a grey-blue, a dusky pink, white and a black outline. There are occasional areas of green, orange and brown-orange. Gold is used sparingly. The text features are painted in a vibrant red and vibrant blue, with the rubric a more orange-red. The ink is black.

Use of Blue

Blue is used liberally in the manuscript as the colour of clothes and drapery, as a ground to figures, and in decorative flourishing, as exemplified by the initials shown in Figure 32 and Figure 41 above. Unsurprisingly, the vibrant blue was found to be lapis lazuli, as shown in Figure 37 below. The peaks at 556 and 1086 cm^{-1} are consistent with published library data that report that the peaks are at 545 and 1096 cm^{-1}. The raw spectrum shows a significant amount of fluorescence, which adds broad features into the baseline spectrum.

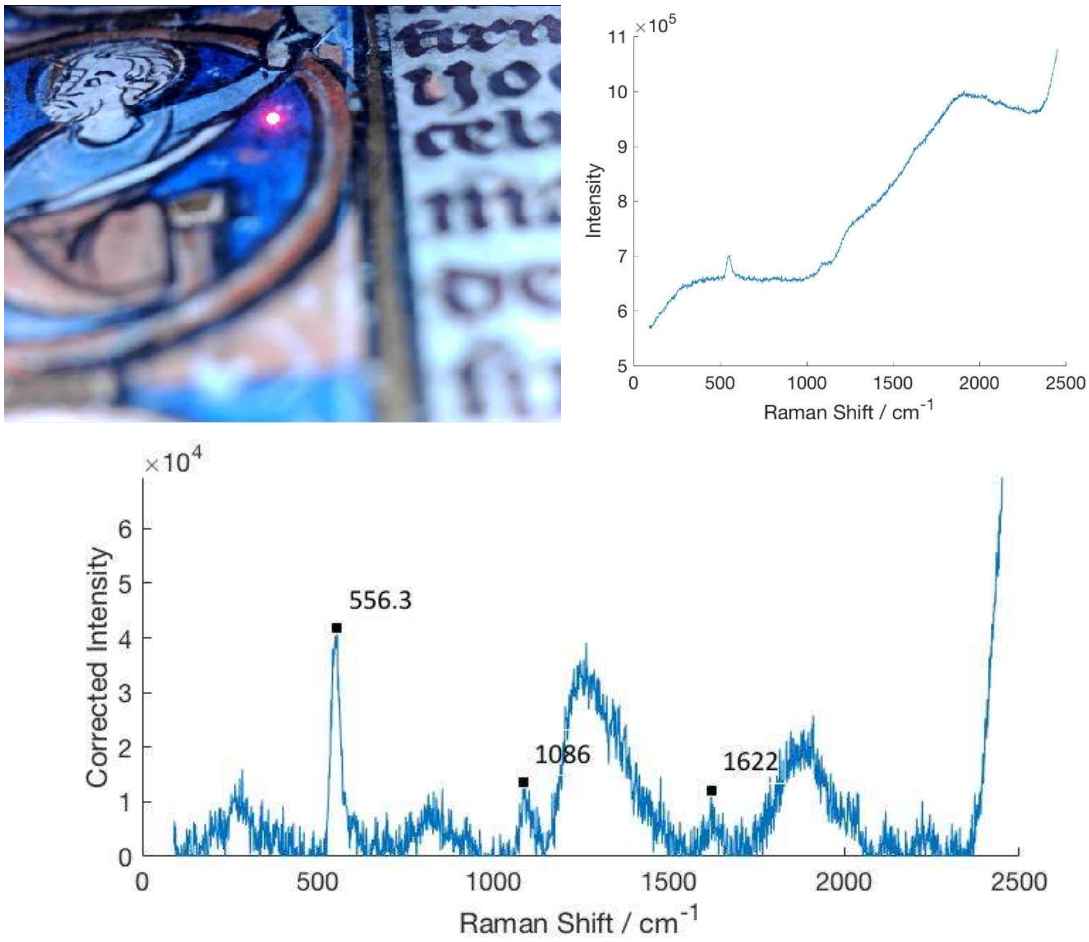

Figure 37: (top left) The spot examined on A.IV.30 fol. 15v, (top right) the raw spectrum obtained and (bottom) the processed and labelled spectrum.

The blue-grey colour used for clothes was also examined, as seen in Figure 38 below, and was found to be lapis ash, a lower grade of lapis lazuli as described in Chapter Two. Lapis ash typically returns fewer peaks than lapis lazuli does, as is the case in below, in which one peak at 556 cm^{-1} emerges from an otherwise fluorescent spectrum. The Raman peak at 556 cm^{-1} is given in published literature as being at 549 cm^{-1} and is due to the symmetric stretching of the S_3^- radical ion - the chromophore that gives lapis lazuli its vibrant blue colour. Resonant enhancement of the spectrum causes overtone bands that are seen up to about 3000 cm^{-1}.[28] Lapis ash has, by its nature, either been more processed than lapis lazuli, and as such has lost some of its vibrant blue chromophores, or is the decoction of a rock with poor lapis lazuli content in, again meaning there are fewer chromophores. Either raw material results in a pigment with a weaker Raman response than that expected in a higher-grade

[28] Esam M.A. Ali and Howell G.M. Edwards, 'Analytical Raman Spectroscopy in a Forensic Art Context: The Non-Destructive Discrimination of Genuine and Fake Lapis Lazuli', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 121 (March 2014): 415–19.

sample of lapis lazuli - hence a smaller peak at 556 cm^{-1} and few or no resonant peaks. In Figure 38 below the raw spectrum is shown labelled and unlabelled, as the peak is easier to distinguish in the raw spectrum, as opposed to the processed spectrum, due to the fluorescence.

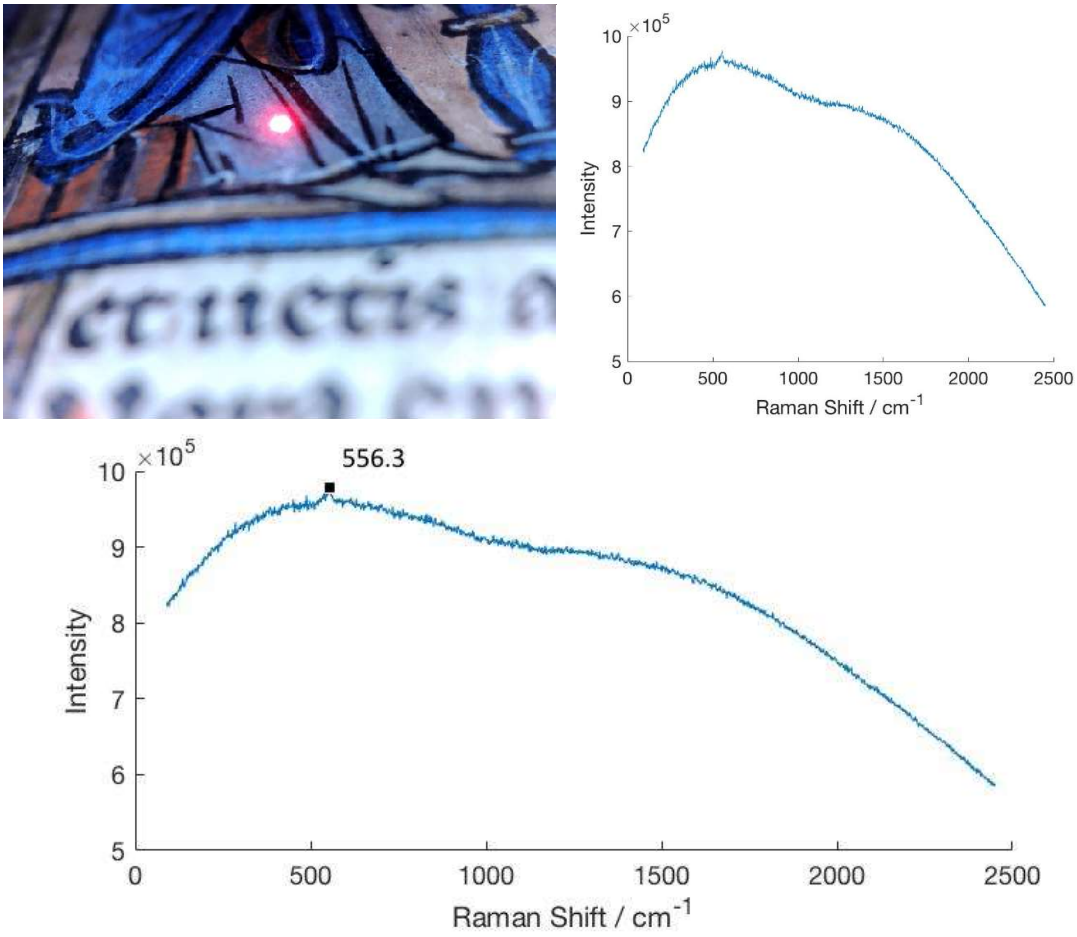

Figure 38: A.IV.30 fol. 12r (left) the spot examined with the Raman system (centre) the raw spectrum obtained and (right) the processed and labelled spectrum.

As mentioned above, had it been possible, the FORS spectra for the folios examined would have been redone, as the system needed realignment and the photomicrographs recorded are dark. However, despite the spectra in Figure 39 and Figure 40 being substandard, they are important as they show that there is no azurite present in either the lapis lazuli or in the lapis ash. A FORS spectrum of a substance that includes azurite has two absorbance bands at 2281 and 2350 nm, and these are not

present in the FORS spectra below, meaning that the lapis lazuli and the lapis ash are not mixed with azurite.[29]

A further indication that the blue colour does not contain azurite can be seen in Figure 35, above, where the blue colour seen under the microscope in white light is rendered 'invisible" under infrared light. Lapis lazuli is transparent in the infrared, whilst azurite is dark.

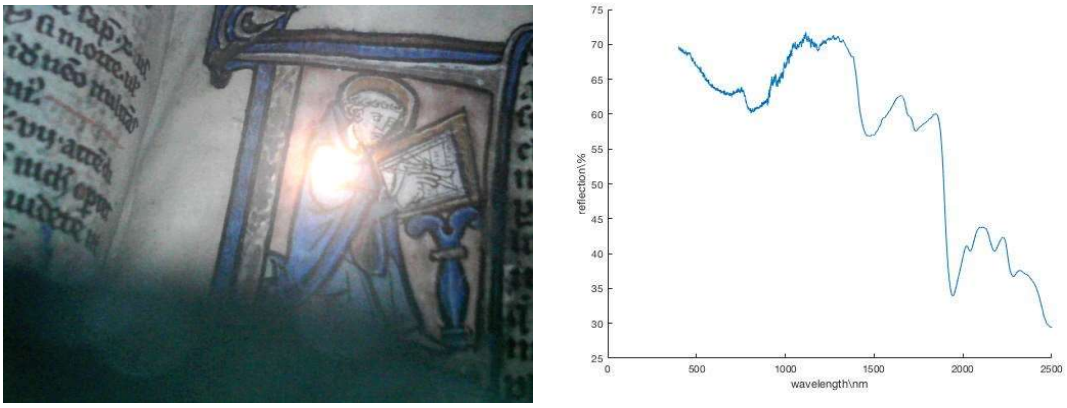

Figure 39: (left) The spot on the blue clothes on A.IV.30 fol. 12r examined by FORS and (right) the FORS spectrum obtained.

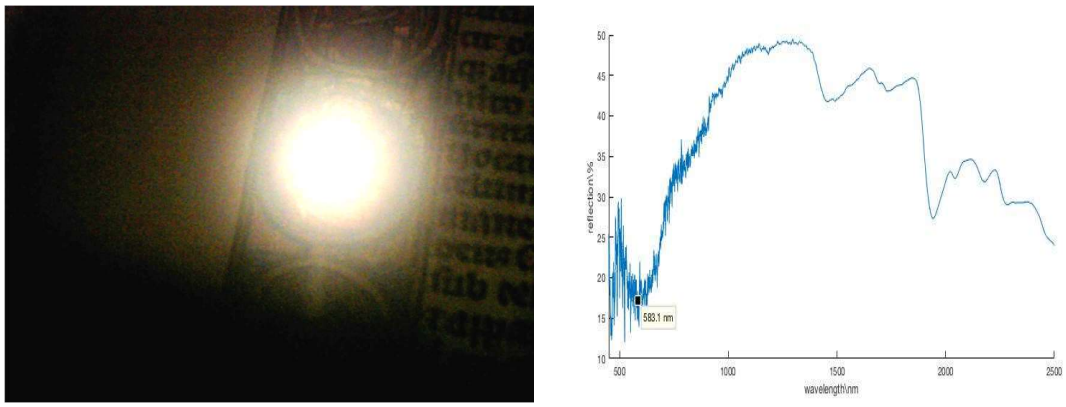

Figure 40: left) The spot on the grey-blue clothes on A.IV.30 fol. 15v examined by FORS and (right) the FORS spectrum obtained.

[29] Delaney et al., 'Use of Imaging Spectroscopy, Fiber Optic Reflectance Spectroscopy, and X-Ray Fluorescence to Map and Identify Pigments in Illuminated Manuscripts'.

Use of Orange

Figure 41: A close up of the historiated initial on fol. 12r of A.IV.30.

Orange is used sparingly in the manuscript, to add details and a flash of colour here and there. In fol. 12r, for example, seen in Figure 41 above, the historiated initial contains a small patch of orange under Jerome's seat. This orange was examined and, as demonstrated by the spectra obtained shown in Figure 42, found to have three peaks at 128, 384 and 555 cm^{-1}. These are consistent with published data for red lead, which state that the Raman peaks are at 121, 390 and 549 cm^{-1}.[30] Again, the labelled raw spectrum is provided, as it is clearer than the processed spectrum.

[30] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts'.

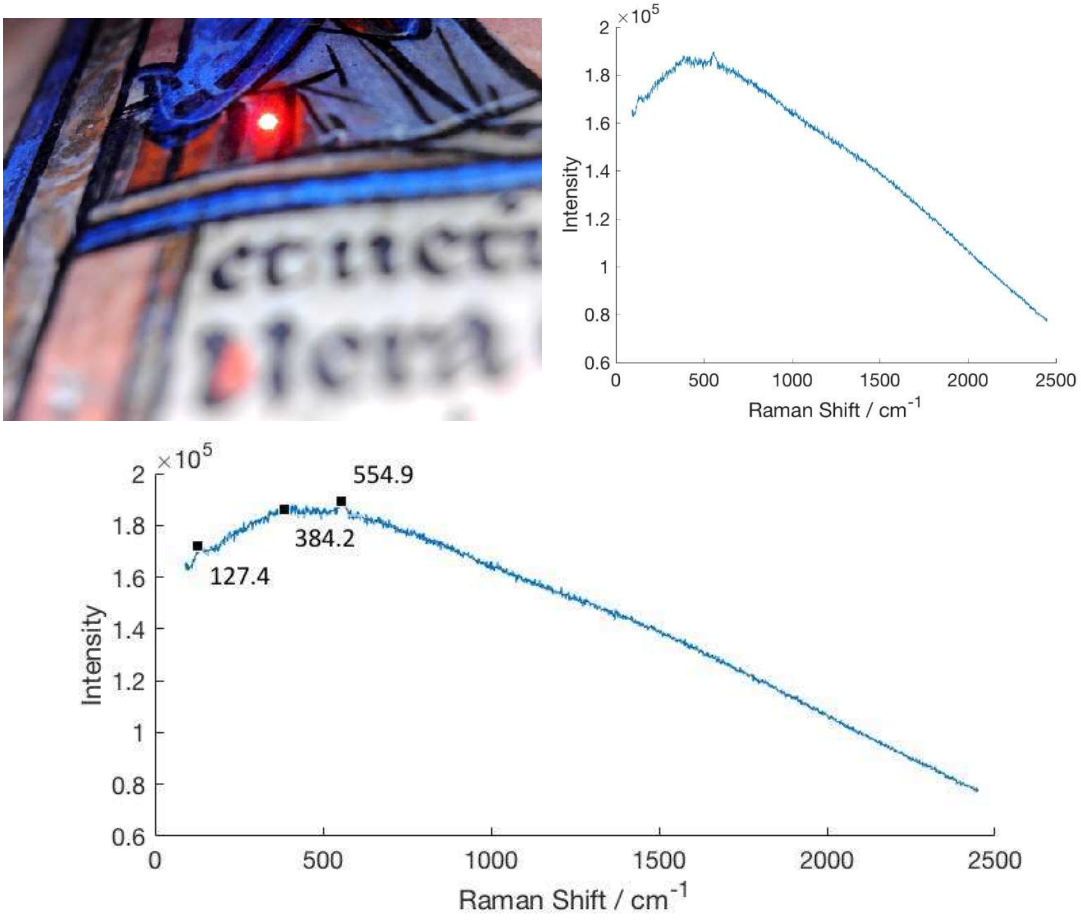

Figure 42: (top left) The spot on A.IV.30 fol. 12r where the orange colourant was examined, (top right) the raw Raman spectrum and (below) the labelled raw Raman spectrum.

On fol. 15v one of the circles (housing a figure) is coloured an orange-brown colour. This was also found to be red lead, as shown in Figure 43 below, with peaks at 130 and 550 cm^{-1} corresponding to the published data peaks mentioned above. The fact that the orange-brown colour here, in Figure 43, is not the same as that of the red lead patch shown in Figure 42 might be because the former features an admixture of another pigment that the spectrometer has not detected, or, more likely, it could be due to the red lead degrading. Red lead commonly degrades in manuscripts to form platternite (PbO_2) or galena (PbS) both of which form a darker coloured pigment, which is what we see here. [31]

[31] Frederik Vanmeert, Geert Van der Snickt, and Koen Janssens, 'Plumbonacrite Identified by X-Ray Powder Diffraction Tomography as a Missing Link during Degradation of Red Lead in a Van Gogh Painting', *Angewandte Chemie International Edition* 54, no. 12 (16 March 2015): 3607–10.

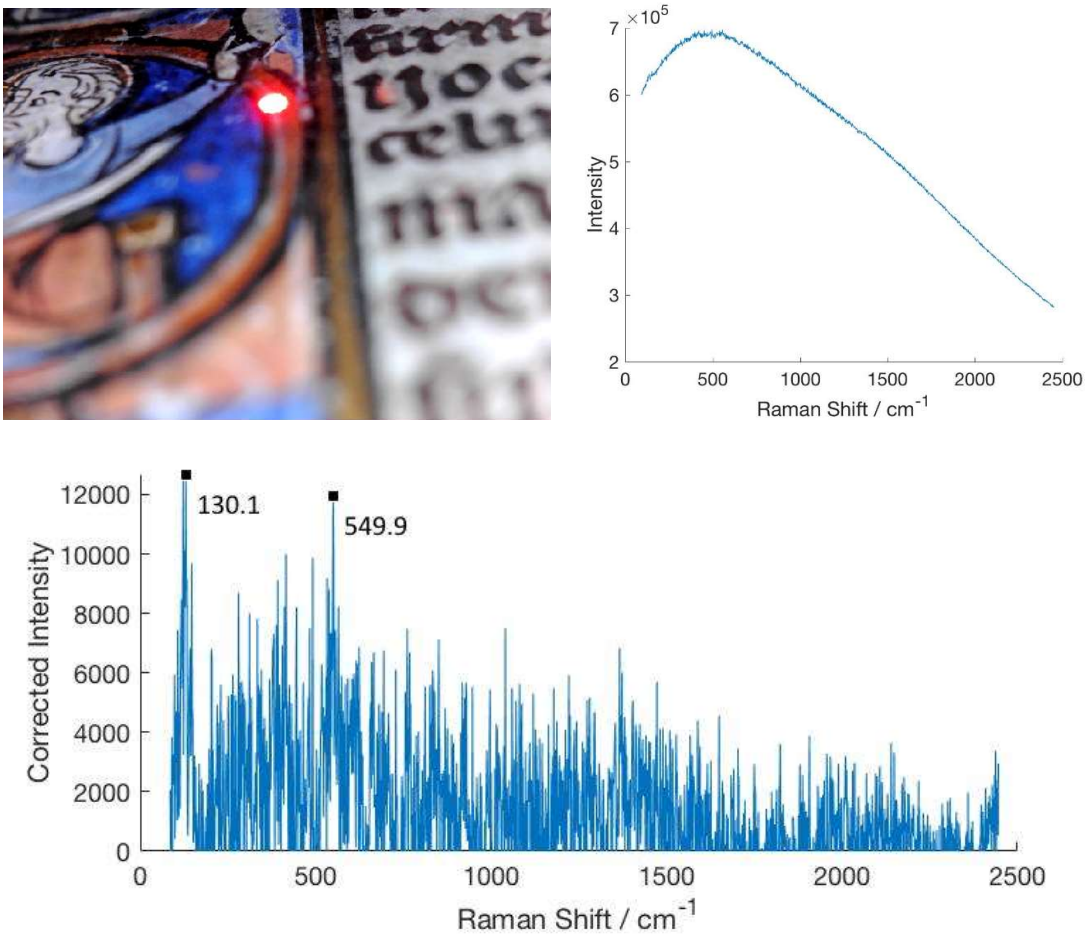

Figure 43: (top left) The spot on the orange-brown circle on A.IV.30 fol. 15v examined by Raman spectroscopy, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

Use of Green

Like orange, green is not seen very often in the manuscript, with only small patches being used where necessary. On fol. 15v a depiction of God separating the land and the sea required a green colour, as shown in full in Figure 32 and close up below in Figure 44. When examined, as seen in Figure 45, the green returned broad peaks centring at 377 cm^{-1} and 1429 $cm^{-1,}$ and the spectrum showed that the laser was being absorbed, which indicates a copper-based pigment. The peak at 377 cm^{-1} is an artefact of the system that is only apparent when there is very little signal - i.e., when the signal is being absorbed. The peak centring on 1428 cm^{-1} does correspond to the peak given in published data for verdigris, at 1438 cm^{-1}. However, the peak obtained in the spectra below is so broad that this is perhaps a tenuous correspondence.

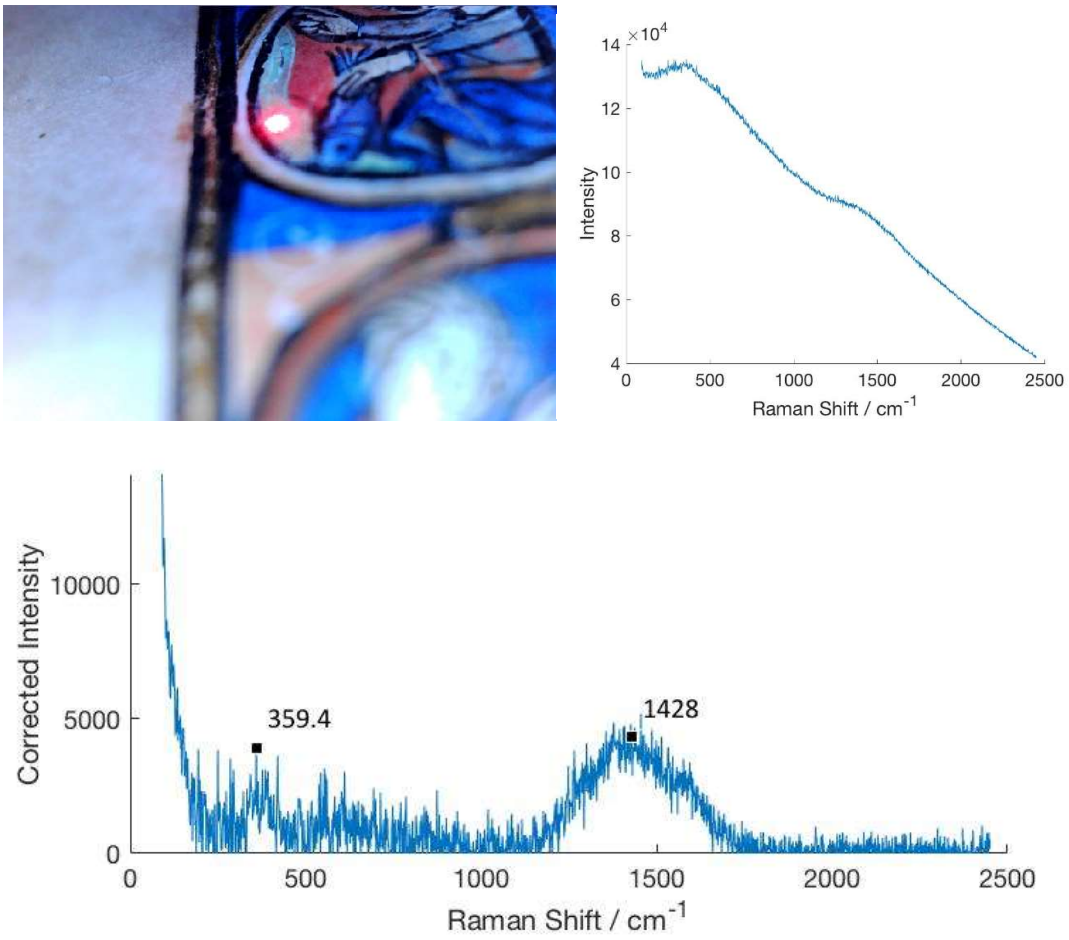

Figure 44: (left) the spot on green of A.IV.30 fol. 15v examined by Raman (centre) the raw spectrum obtained and (right) the processed spectrum.

Fortunately, the FORS spectrum, shown in Figure 45 below, does offer some further insights into the nature of the pigment, as it shows an absorbance maximum of 721 nm. This is consistent with the published absorbance maximum for verdigris, reported at 720 nm.[32]

[32] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p.1491.

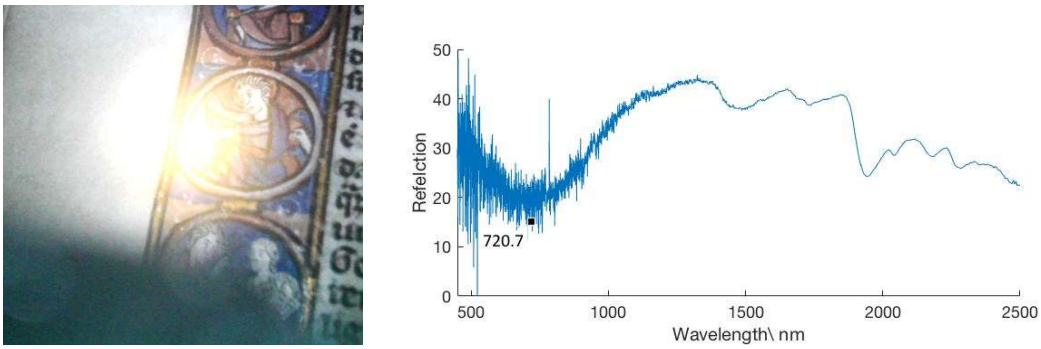

Figure 45: (left) The spot on A.IV.30 fol. 15r examined by FORS and (right) the spectrum obtained.

Use of black

As mentioned, black was used often in the manuscript, to outline figures and other artwork. This means that despite its ubiquity, it is not easy to obtain by Raman spectroscopy, as its lines are usually too thin to yield satisfactory spectra. Similarly, for the FORS system, with its larger field of measurement, the problem is even more acute.

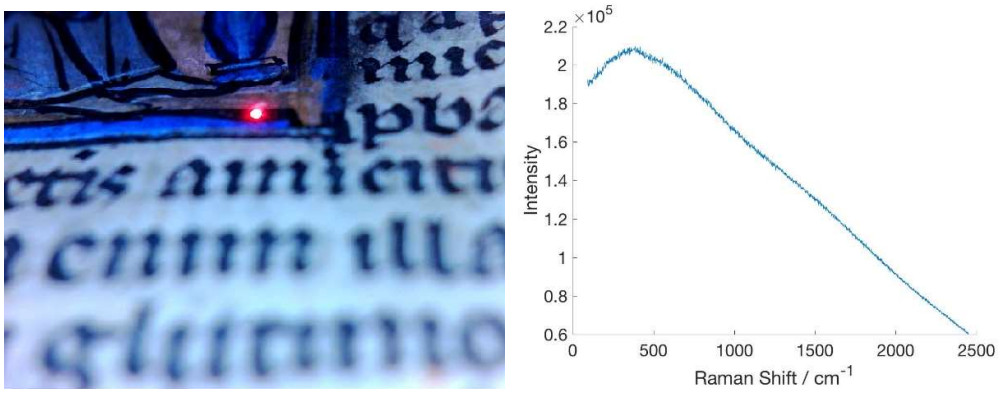

Figure 46: (left) The spot on the black line of A.IV.30 fol. 12r which was examined and (right) the raw spectrum obtained.

The spectrum recorded for the black used in a line on fol. 12 (shown in Figure 46 above) does not offer any clues as to what the pigment is, even when processed. However, as seen in Figure 47, when the face of Jerome on fol. 12r is illuminated with infrared light and viewed through a microscope, the black lines are still dark, which suggests that the lines are carbon, as carbon remains dark under infrared illumination. If the line were indigo, which is sometimes used to draw dark lines, then the lines would be light when illuminated with infrared wavelengths.

In addition, in every manuscript examined so far in this project, the black lines have been carbon - so it is not unreasonable to suggest that this line is carbon too.

Figure 47: An infrared image of the historiated initial on fol. 12r.

Use of pink

Like the black above, the Raman spectrum of the pink area examined does not yield any peaks to allow its identification, as seen in Figure 48 below. However, pink is deployed in a different way to black: it was deployed as infill behind figures and shapes and therefore has a wider coverage and so is easier to examine with the FORS system. Unfortunately, the FORS spectrum recorded was erroneous and therefore did not offer any further information as to the identity of this colour stuff.

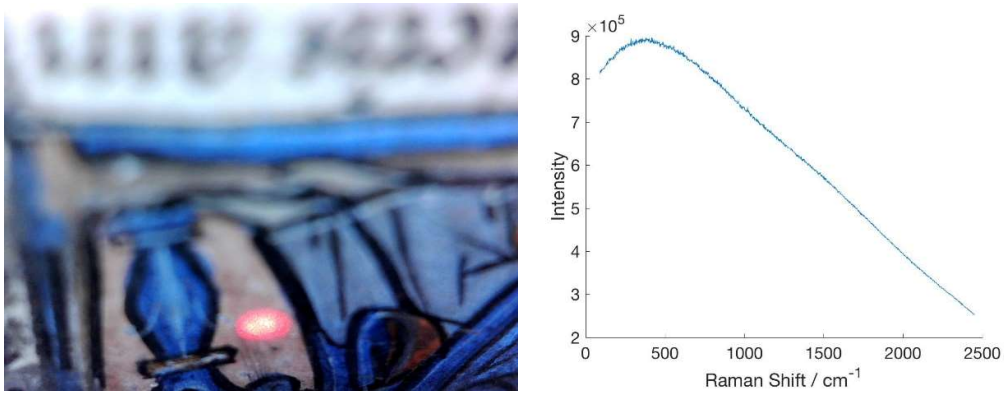

Figure 48: The spot on the dusky pink of A.IV.30 fol. 12r examined and (right) the spectrum obtained.

Use of White

White (like pink and blue) is used fairly often in the manuscript - for faces and flesh, as well as on objects. Figure 49 shows the Raman spectrum obtained when a patch of white on the body of the sleeping Adam in an historiated initial was examined.

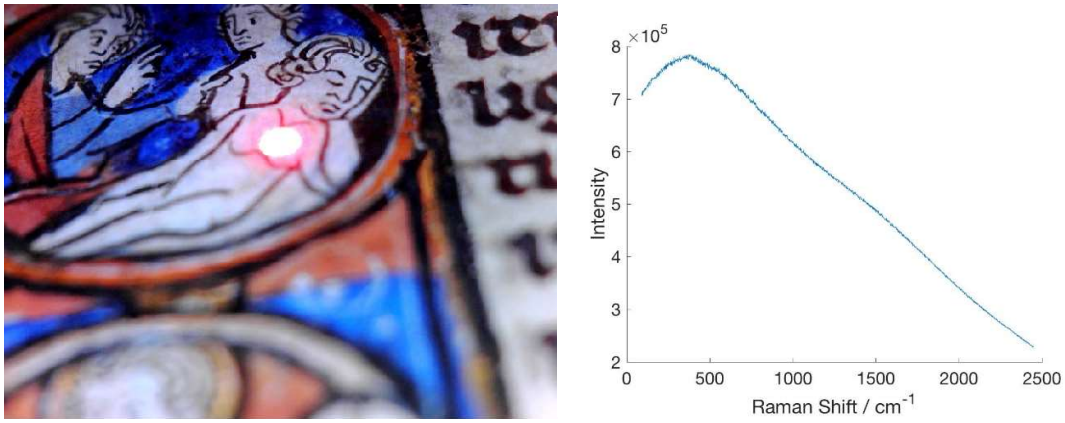

Figure 49: (left) The spot on A.IV.30 fol. 15v where the white was examined, and (right) the raw spectrum.

Despite being able to see a very small peak at 105 cm^{-1} in the raw spectrum, which would be indicative of white lead, the processed spectrum does not reveal this peak (and so is not included).

However, it is highly likely that this pigment is white lead, as it is a stable, easily available pigment found in many manuscripts of this age, and has been seen often in the manuscripts in this project. The FORS spectrum seen below in Figure 50**Error! Reference source not found.**, although erroneous in the visible range, also supports the notion that this pigment is white lead, with a strong absorbance peak at 1445 nm, which is indicative of white lead.[33]

[33] Mulholland et al., 'Identifying Eighteenth Century Pigments at the Bodleian Library Using in Situ Raman Spectroscopy, XRF and Hyperspectral Imaging', p.11.

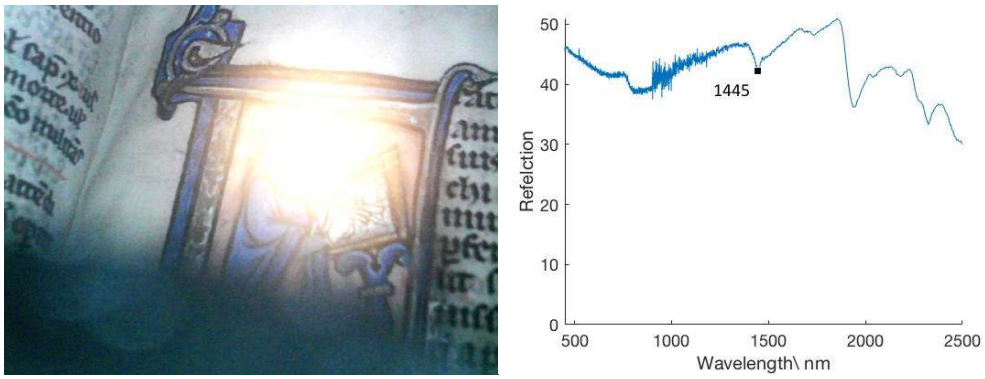

Figure 50: (left) The spot on A.IV.30 fol. 12r examined and (right) the resulting FORS spectra.

Use of Gold

Gold occasionally features in the manuscript; its deployment is not opulent. It was employed to colour thin borders, seen most clearly in Figure 4 and Figure 5 above, and as a highlight to important figures depicted, as seen in Figure 51 below where Jerome's halo and writing board are covered in gold. Jerome's beard and hair even seem to have a touch of gold on them, and it is difficult to ascertain, even with the microscope, if this is deliberate.

As gold is so reflective and does not yield a Raman spectrum at the low powers used in manuscript work, no spectra were taken to confirm that the pigment was gold or to evaluate its purity; however, it can be reasonably be assumed from its appearance under the microscope, and from its use in comparable manuscripts that the gold in the manuscript is indeed the metal.

Figure 51: Photomicrograph of the use of gold around Jerome's head from fol. 12r.

Text and text ornamentation

Text

The neat black text was examined on fol. 12r with both the Raman and FORS systems. The Raman spectrum returned gave no indication of the presence of carbon, as seen in Figure 52 below. The FORS spectrum, in Figure 53 below, supports this and indicates that the ink is gallotanic.

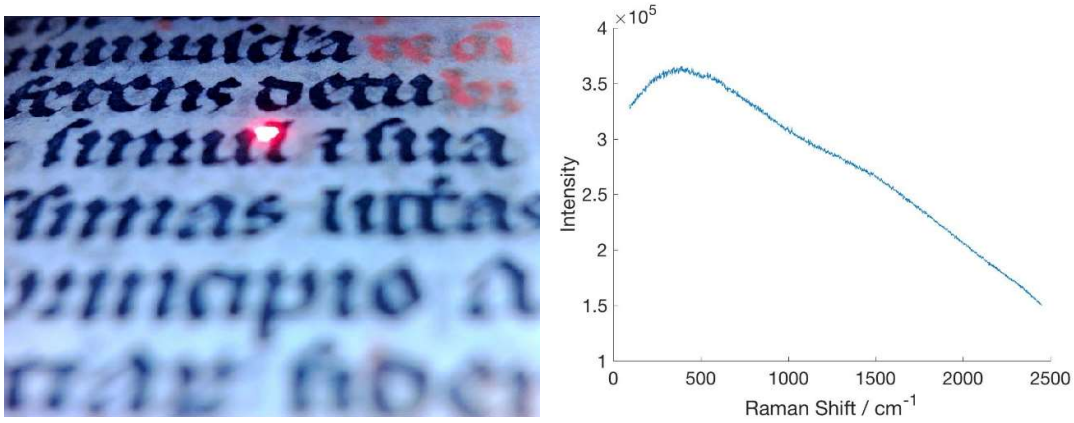

Figure 52: (left) The spot on A.IV.30 fol. 12r examined by Raman spectroscopy and (right) the raw spectrum obtained.

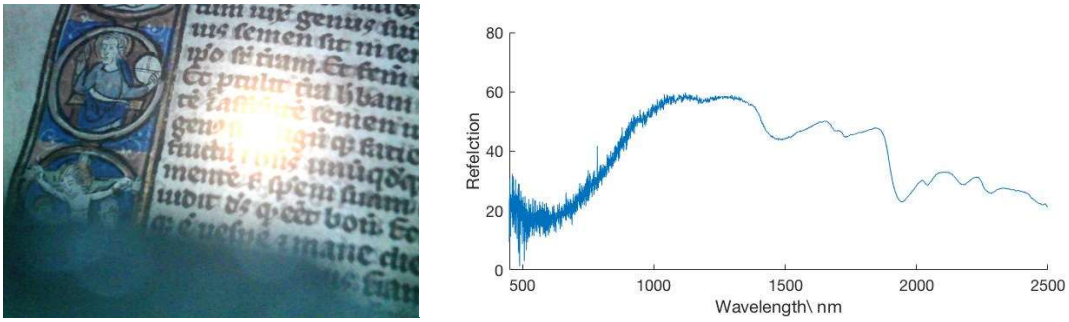

Figure 53: (left) The spot on A.IV.30 fol. 15r examined by FORS and (right) the spectrum obtained.

Flourishing

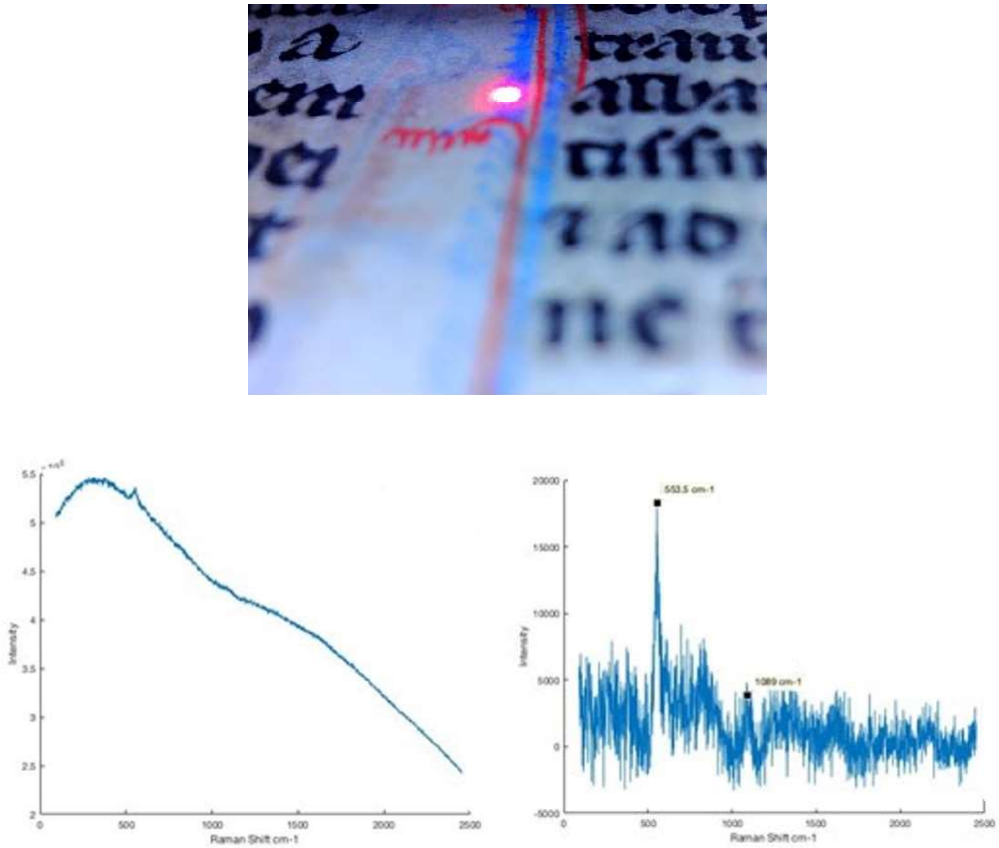

Figure 54: (top left) The spot on A.IV.30 fol. 12r examined by Raman, (top right) the raw spectrum, and (below) the processed spectrum.

The blue flourishing, a light but vibrant blue, is lapis lazuli, evidenced by the spectra in Figure 54 above, with Raman peaks at 554 and 1089 cm^{-1}, which are consistent with the peaks given in published data at 545 and 1096 cm^{-1}. Unusually for a lapis lazuli spectrum, the peaks emerge from a strongly fluorescent background, which could be from the binder it is mixed with to make the paint.

Running heading /chapter headings

Like the blue in the flourishing described above, the blue in the running heading on fol. 12r is also lapis lazuli and also displays an unusual amount of fluorescence, which accounts for the broad peaks in the baseline plot. Here the peaks are at 557 and 1086 cm^{-1}.

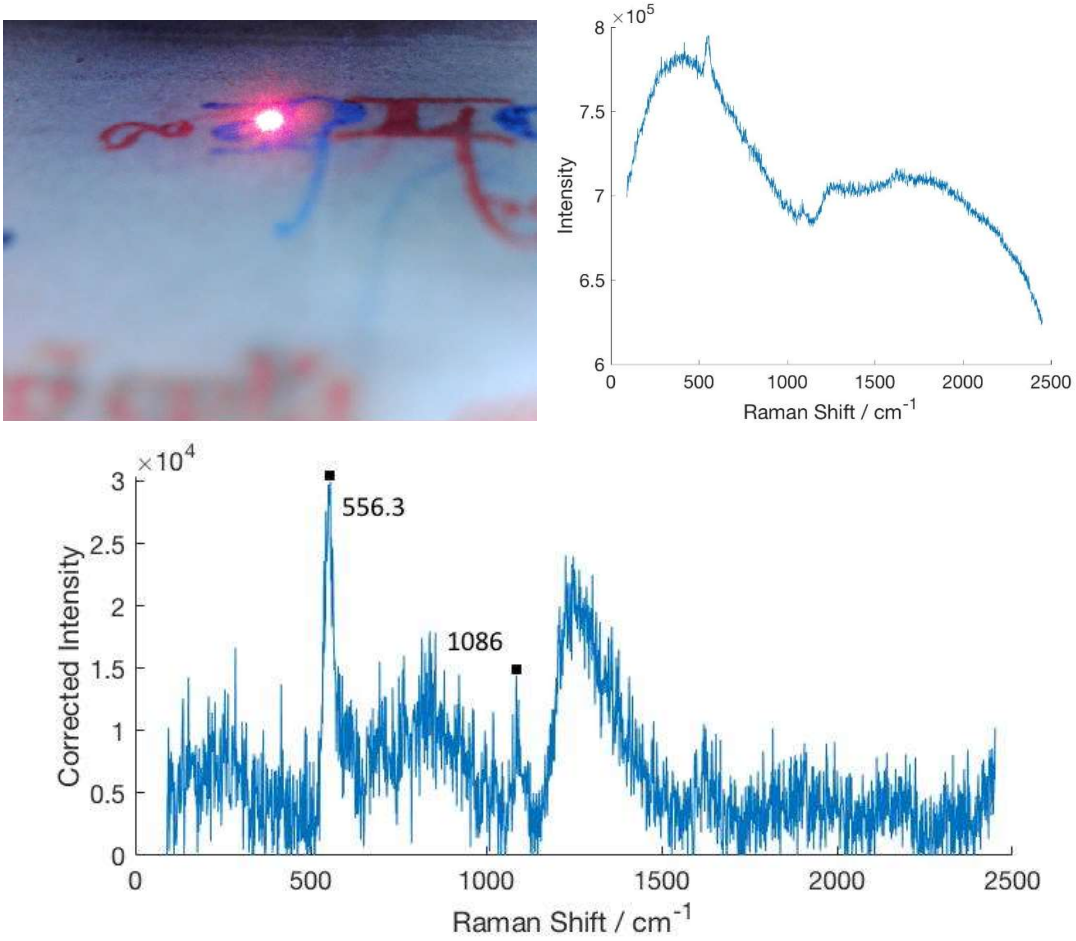

Figure 55: (top left) The spot on A.IV.30 fol. 12r examined by Raman spectroscopy, (top right) the raw spectrum and (bottom) the processed spectrum.

Rubric

The orange-red rubric at the top of fol. 12r, previously shown in full in Figure 31, is examined close up in Figure 56. With peaks at 258 and 348 cm^{-1}, the pigment is vermilion, which is cited in published literature as having peaks at 251 and 342 cm^{-1}.[34] Unusually for vermilion, the raw Raman spectrum is not particularly intense and shows fluorescence, which again could be attributed to the binder in which it is mixed.

[34] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 11.

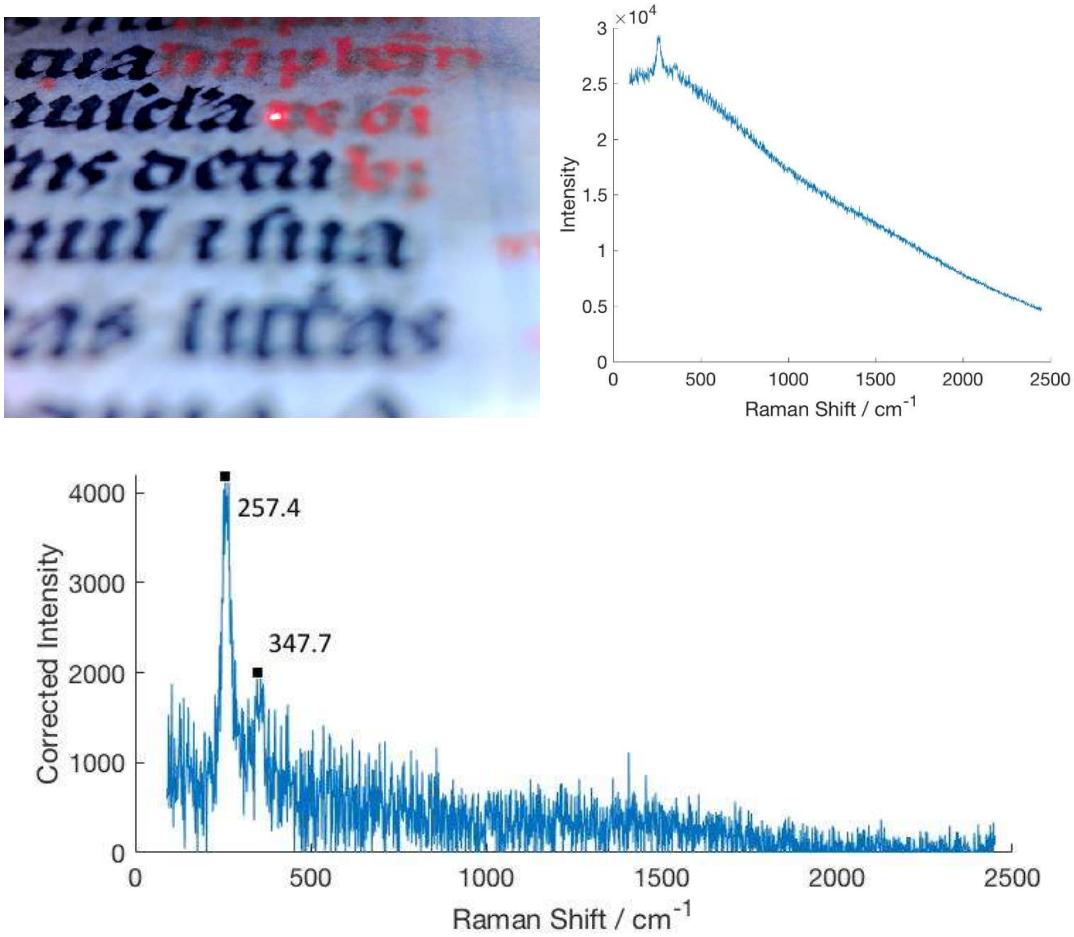

Figure 56: (left) The spot on DUL A.IV.30 fol. 12r examined by Raman (centre) the raw spectrum and (right) the processed spectrum.

Further comments on the palette as a whole

That the palette of the artwork on the folios examined reveals the use of pigments already commonly known to be employed and holds no surprises. The vibrant blue used both in the decoration and in the text ornamentation is lapis lazuli with no traces of the cheaper azurite mixed in. The grey-blue is lapis ash, the white is white lead, and the black in the artwork is likely carbon, with the black text probably gallotanic ink, with no inclusion of carbon.

The occasional areas of green are certainly copper-based and are probably verdigris; the orange areas are red lead, so too are the brown-orange areas. Vermilion provides the red-orange text and, although not examined, is likely to provide the vibrant red in the text ornamentation as well. An organic pink is employed, similar to that seen in the other manuscripts examined so far. Gold was used in both initials examined.

Durham Cathedral Library A.IV.37

Description and provenance

Durham Cathedral Library A.IV.37, also known as The Auckland Bible (after one of its late medieval Durham owners, as explained below), is a thirteenth-century bible in the Paris style, made in England in the middle part of the century. Measuring 236 x 152 mm, the manuscript is hardly 'pocket-sized' (as seen in Figure 57), although is still portable and is diminutive when compared to those bibles made for the lectern - A.II.3, for example. The manuscript is in a seventeenth-century binding.

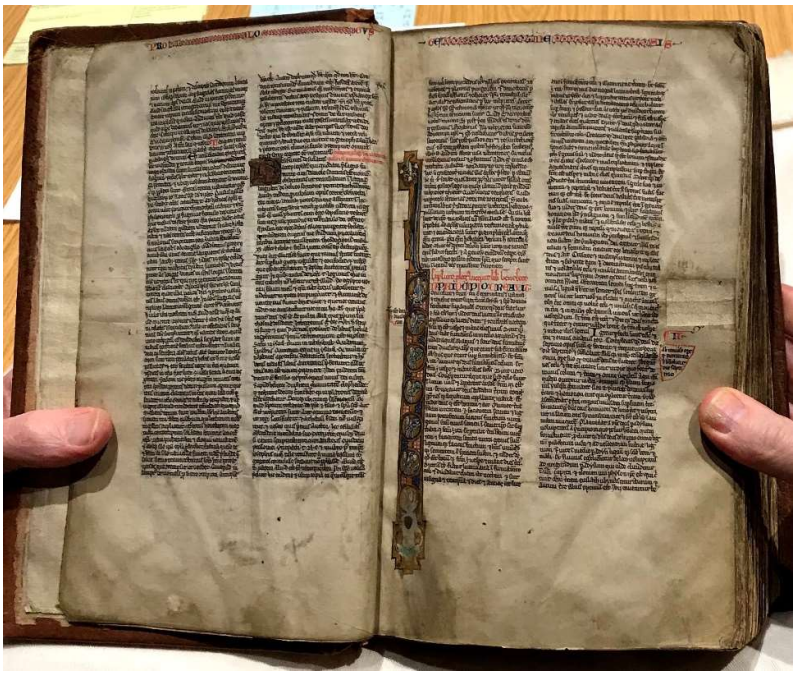

Figure 57: DCL A.IV.37, fols. 4v and 5r.

Having only been obtained by Durham Cathedral in 2005 when bought at auction, it is in fact a reacquisition, as the manuscript was part of Durham Cathedral Priory Library in the fifteenth century.[35]

In between its stints as a Durham Cathedral manuscript, the book belonged to The Willoughby family, who were the Lords Middleton of Wollaton, and was kept in the Middleton deposit at Nottingham University Library. How the manuscript came to be part of the Middleton collection is unknown,

[35] Gameson, *The Medieval Manuscripts of Durham Cathedral: A Descriptive Catalogue (in Progress)*.

although there are connections between the first Lord Middleton and Thomas Man Jr who owned many Durham Manuscripts, so it may have been acquired from him. [36]

Previous to being a Durham Priory book the manuscript belonged to John Auckland (who lends the book its name), a monk of Durham c.1450-1494 and prior 1484-94, who was given it by Richard Bell, a monk of Durham c.1426-1478 and prior 1464-1478. Before that, it belonged to Thomas Launcells, a monk of Durham c.1355-1408/9, and prior to that, it had some association with Robert Greystanes, a monk of Durham c.1304-1333/4, and subprior 1332/3.[37]

Although its place of manufacture is unknown, it was more than likely made for use in East Anglia or Ely as the prominent commemorations of Etheldreda and Sexburga in the calendar attest.[38]

The manuscript contains The Bible and prologues in the standard 'Paris Bible' order with the exception of Colossians, which follows, rather than precedes, Thessalonians I and II as is normally the case. Standard chapter divisions are marked in some books and not in others - in those without, some have been subsequently amended in full or in part.

Following the Bible is a calendar on two folios - laid out with 6 months per page. This is the most compact calendar examined in the project thus far, as most manuscripts give each month its own page. After the calendar is a concordance to the gospels - a cross-referencing system where events in one gospel are linked by chapter numbers and/or reference letters to similar events in other gospels. In this manuscript, events are referenced with both chapter numbers, where available, and a reference letter which should correspond to a letter in the margin of the main text. However, the letters are defunct in this correspondence as there are no markings in the main text. The letters probably appear as they have been copied, without thought, from an anterior manuscript. Furthermore, the entries for the concordance are out of order in places, and some material from the list of vocabulary (described below) is duplicated in the middle of the section. The disorder seems due to copying errors and not rearrangement of folios after completion, as there are some attempts to rectify the mistakes with notes and crosses in the margin and gutter (some now torn away). [39]

The last section of the manuscript is a list of vocabulary with blocks of entries for each letter in four columns per page.

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[36] Gameson, *The Medieval Manuscripts of Durham Cathedral: A Descriptive Catalogue (in Progress)*.
[37] Gameson, *The Medieval Manuscripts of Durham Cathedral: A Descriptive Catalogue (in Progress)*.
[38] Gameson, *The Medieval Manuscripts of Durham Cathedral: A Descriptive Catalogue (in Progress)*.
[39] Gameson, *The Medieval Manuscripts of Durham Cathedral: A Descriptive Catalogue (in Progress)*.

Codicology

Quire formation

Fronted by a quire of 2 medieval flyleaves most of the quires are in 12s or 10s with one 13 (a 12 plus a singleton added), one 11 (a 12 with one leaf cancelled) and one 5 (which was a 6 with one leaf missing). The calendar is in a quire of 2, showing that it was added as a separate phase of work.[40]

Parchment

The parchment of the manuscript is of moderate quality but is even-toned, although is now weathered and scuffed through use. The folios are arranged with the hair sides facing, and thus the flesh sides facing. That the hair and flesh sides can be distinguished informs us that the technology that allowed the parchment to be made as thin as possible has not been employed to its maximum capacity here. There are many little flaws and tears throughout the manuscript, and, although many are repaired, the repairs are with poor quality or recycled parchment.

Using imperfect parchment to make a manuscript suggests that either the manuscript was made in some place or time where parchment supply was scarce, or more likely in this case, that the choice of mediocre parchment reflects the need for economy. The inclusion of sub-standard work, as evidenced in the concordance to the gospels above, is a further indication of the notion that this manuscript was not produced to the highest possible grade.

Damage

There are a few places where there has been liquid damage, and two creases - on fols. 344 and 345. As mentioned above, there are numerous small tears and flaws throughout the manuscript.

The bottom of the initial on fol. 5, described below, has been defaced as seen in Figure 58.

[40] Gameson, *The Medieval Manuscripts of Durham Cathedral: A Descriptive Catalogue (in Progress)*.

Figure 58: A.IV.30 fol. 5r - the defaced section of the initial.

Text layout, ornamentation and rubrics

The text is arranged in two columns of width 44 mm, with the overall text block measuring 155 x 96 mm. There are 60 lines scored in lead and 60 lines of text. Pricking was done by awl or knife.

Script and hands

This manuscript is written mainly in Textualis semiquadrata, although some of the corrections could be said to be almost Anglicana. The number of hands is uncertain as the manner of the script changes in each section of the book described above; sometimes the script is informal, sometimes the ascenders are elongated, sometimes the script is more compact. These changes may be due to the scribe changing their script to economise to the space provided, or they could be indicative of different hands.[41]

Artwork

Style of artwork

As seen in Figure 59, the historiated initial on fol. 5r is set against gold and runs two-thirds of the page. The initial is painted in a similar style to that seen in A.IV.30. This fol. is the start of the book of Genesis and features the days of creation and what was presumably the devil, although this has been spoiled, as shown in Figure 58 above.

[41] Gameson, *The Medieval Manuscripts of Durham Cathedral: A Descriptive Catalogue (in Progress)*.

Figure 59: A close up of the historiated initial on A.IV.37, fol. 5. The initial is about 15 cm high.

A few other initials are decorated in the late Channel style, the grandest of which can be seen in fol. 3. The Channel style evolved in England and the Channel region in the late twelfth century and was, by the thirteenth century, ubiquitous.[42] The style employs strong colours, fleshy leaves with spindly stems and small white dog-like or leonine creatures.[43]

Simpler decorated initials, as seen in Figure 60, are rendered in gold, pink and blue, herald the start of most of the other Biblical books, some of the Psalms, and the first two prefaces.

[42] Walter Cahn, 'St.Albans and the Channel Style on England', in *The Year 1200: A Symposium* (New York: Metropolitan Museum of Art, 1975), 187–230.

[43] 'Glossary', The British Library (The British Library), accessed 15 April 2020, https://www.bl.uk/medieval-english-french-manuscripts/glossary.

Figure 60: DUL A.IV.37 fol. 337r.

Red and blue flourished initials (see a blue example, flourished in red in Figure 60 above) signify the start of other chapters, individual psalms, and many prologues. Other prologues and the initials for each Biblical book listed in the list of chapters are red or blue flourished in the other colour. The 'KL' monograms at the top of the calendar are decorated with one red letter and one blue letter, with flourishing in the other colour. Chapter initials are in plain red or blue with running headings in alternate red and blue letters; chapter numbers are alternately red and blue numerals with paraphs.

The concordance to the Gospels only has rubrication and no other colour, and the vocabulary list has no colour.

Approach to painting

In contrast to the story of economy indicted by the mediocre parchment and disordered writing, the application of paint seems to be diligent and practised. Investigations with the microscope reveal details in the painting that might not otherwise ever have been noticed.

Figure 61 illustrates the careful attention paid to the depiction of the clothing. A lighter and a darker blue are used, along with black lines of varying thickness to denote creases and folds, and a barely perceptible white line is added as a highlight. Similar treatment is given to the creation - black and white lines accentuate two shades of blue and two shades of green - which is remarkable in a small section of an initial measuring no more than a centimetre. The face also is given considered treatment, with confident lines articulating the features and dabs or red accentuating the cheeks and lips.

A few details do stop the painting being considered perfect, however. The hand grasping the foliage might be said to be clumsily painted, as the lines between the fingers are very thick, and the hand itself seems oversized. In addition, the microscope allows us to see that the application of gold leaf is flawed. Some of the leaf may have moved since application, but some, for example the gold that is around the top of the head, seems to have been added as an afterthought. The gold next to the figure's back seems to overlap some of the drawing too.

Approx. 1 cm.

Figure 61: A photomicrograph of a section of fol. 5r; God creating the land and vegetation.

Palette

Overview

As seen from Figure 61 above and Figure 62 below, the palette in A.IV.37 is limited, but used creatively. Blue, in various shades, features heavily - as does dusky pink. There is a little use of a dark and a light green, a blue-grey, an orange, white lines and black lines. Text ornamentation is red and blue. Gold features often, especially when compared to its limited use in A.IV.30.

Use of Blue

Approx. 1 cm.

Figure 62: A.IV.37 photomicrograph of part of the initial on fol. 5r.

As seen in the robes of God in the initial on fol. 5r (Figure 62), blue is deployed in both light and dark shades with white and black lines to add detail and tone. Also shown in the bottom left corner is a more vibrant blue that colours the ground to the initial (reproduced in full in Figure 57 and Figure 59).

The vibrant blue colouring of the initial was examined by both FORS and Raman spectroscopy. As can be seen in Figure 63, the blue contains lapis lazuli with the peaks at 556, 1096 and 1627 cm^{-1} clearly visible in the processed spectrum, which correspond to those in published data (at 545 and 1096 cm^{-1}).[44]

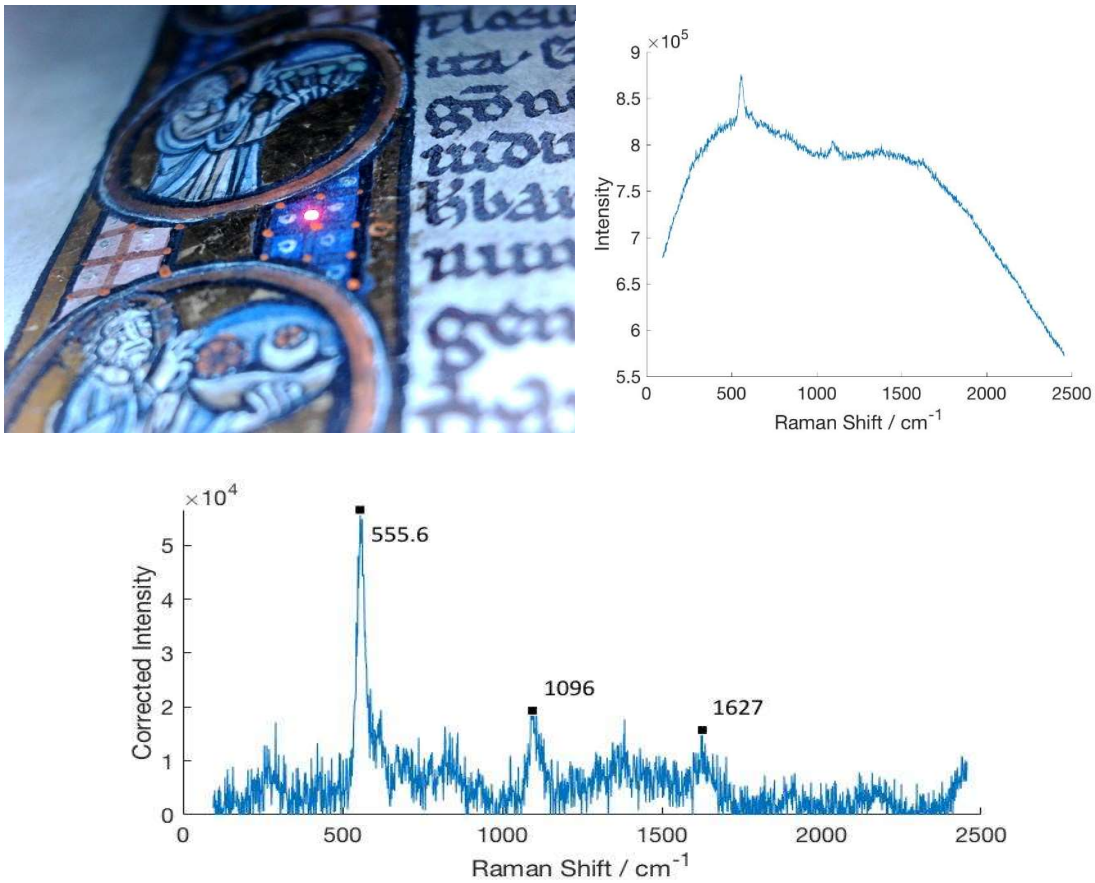


Figure 63: (top left) The spot on fol. 5r where the vibrant blue was examined, (top right) the raw spectrum obtained and (below) the processed spectrum.

The FORS spectrum, taken from a blue spot at the bottom of the initial as seen in Figure 64, shows an absorbance maximum at 613 nm, confirming the presence of lapis lazuli in the blue colourant.[45] The fact that there are no absorption bands at 2285 and 2352 nm indicates that azurite is not present.[46]

[44] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p.1222.
[45] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p.1491.
[46] Mulholland et al., 'Identifying Eighteenth Century Pigments at the Bodleian Library Using in Situ Raman Spectroscopy, XRF and Hyperspectral Imaging', p. 11.

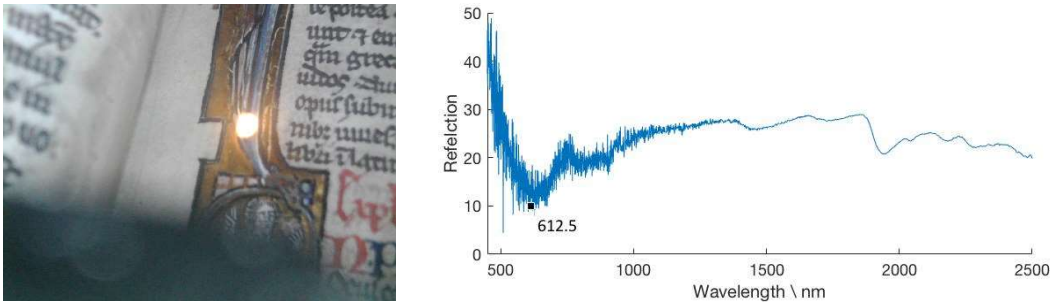


Figure 64: (left) The spot on A.IV.37 examined by FORS and (right) the spectrum obtained.

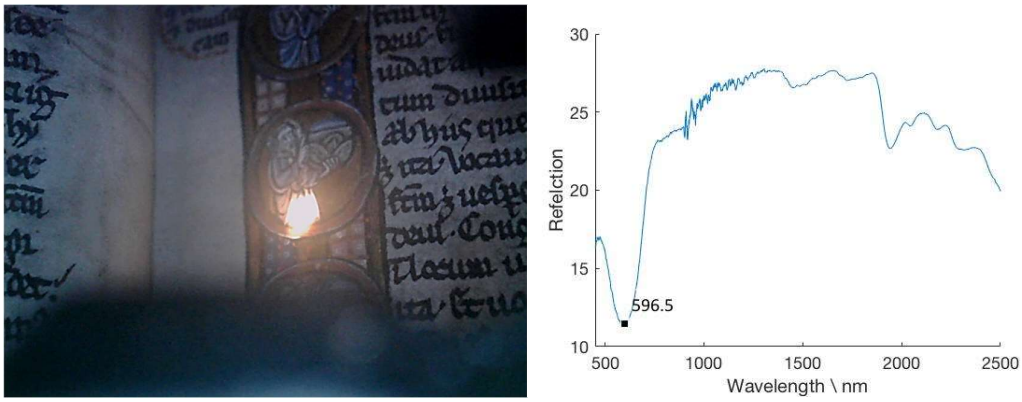


Figure 65: (left) The spot on DUL A.II.37 fol. 5r that was examined by FORS, and (right) the spectrum obtained.

As seen in Figure 65, another patch of blue pigment was examined by FORS, and the resulting spectrum indicated that this was lapis lazuli, with an absorbance maximum at 597 nm, which is consistent with that in published data for lapis lazuli, at 600 nm.[47]

To confirm that the use of lapis lazuli was not limited to the grander initials another, more prosaic, initial was examined, on fol. 337r. The full initial can be seen in Figure 60. As seen below in Figure 66, the spectra obtained have peaks 282, 561 and 1098 cm^{-1}, which correspond to that for lapis lazuli in

[47] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

published works where the peaks are given as being at 286, 545 and 1096 cm^{-1}.[48] Fol. 18r was also examined, and again, the blue was found to be lapis lazuli.

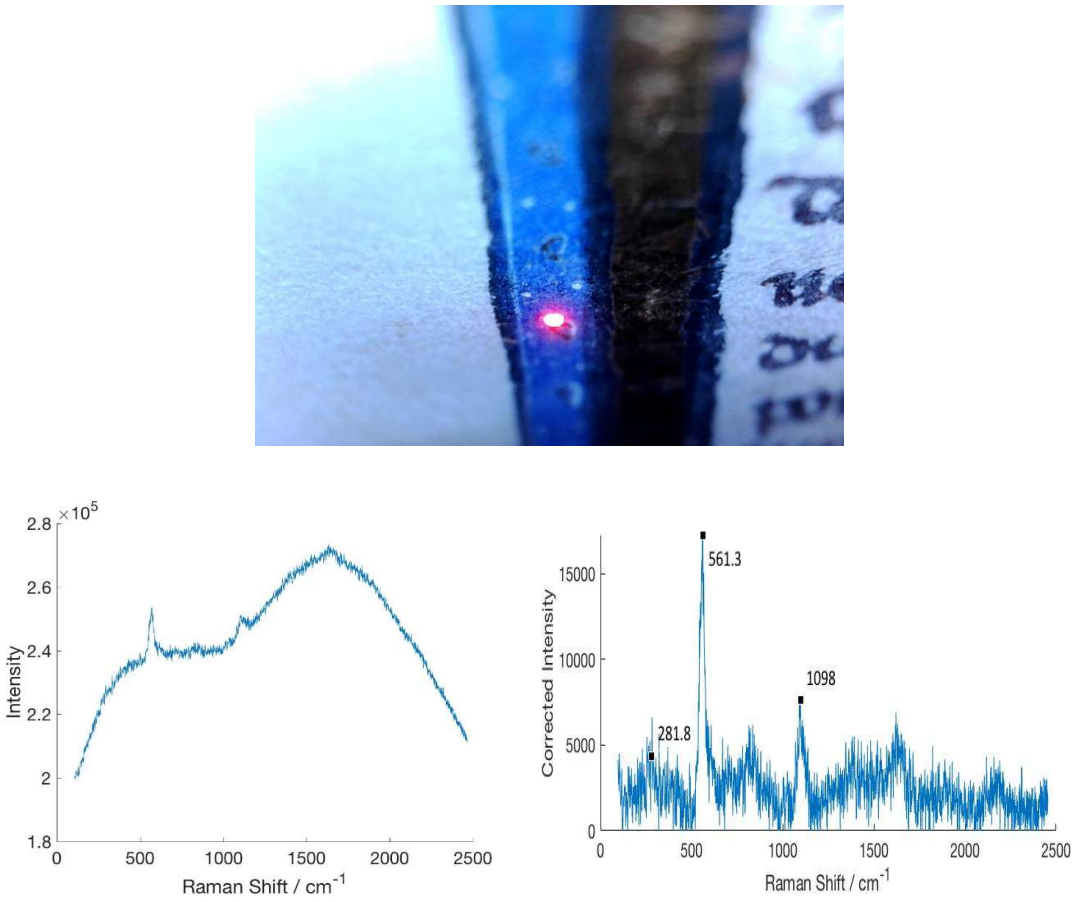


Figure 66: (top) The area of A.IV.37 fol. 337r examined with (left) the raw spectrum obtained and (right) the processed spectrum

Aside from the vibrant blue, there is also a duskier, pale blue-grey, seen clearly in Figure 62. This colour was also examined, as shown in Figure 67 and found to be lapis ash. The peaks at 546, 1096 and 1650 cm^{-1} correspond to those in published data for lapis lazuli. As discussed in Chapter Two, lapis ash is a duller blue-grey by-product of the vibrant lapis lazuli but still shows the characteristic bands of lapis lazuli in the Raman spectrum.

[48] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

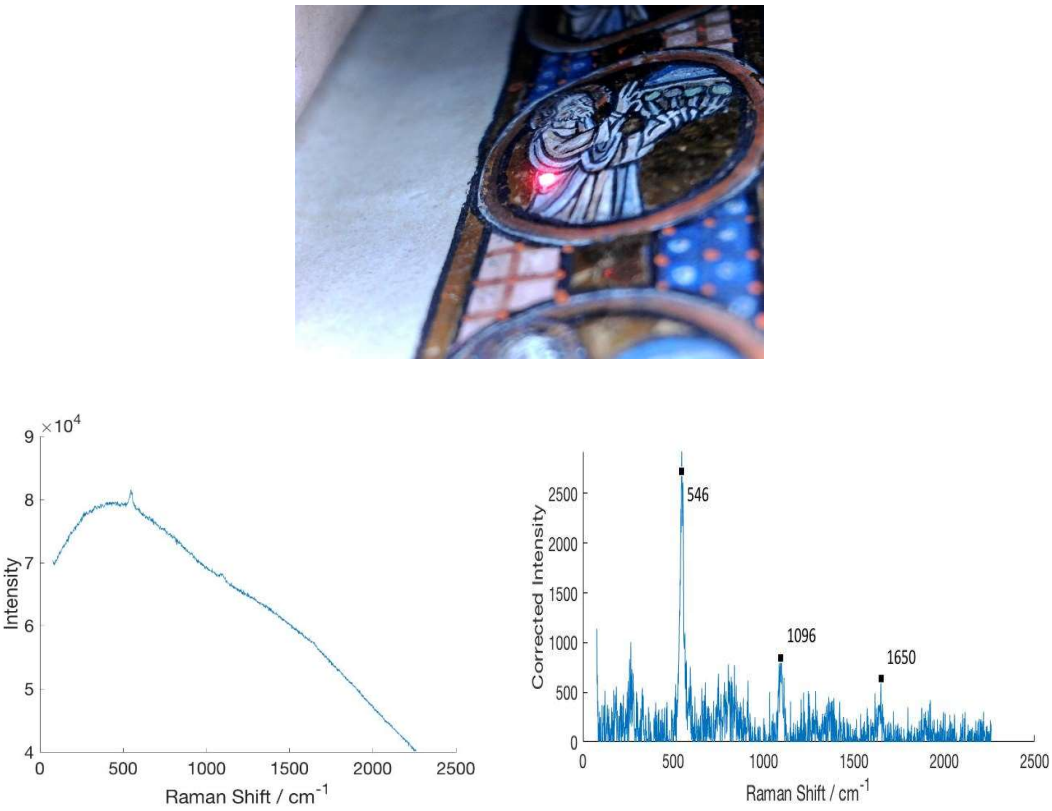


Figure 67: (top) the blue-grey area on A.IV.37 fol. 5r that was examined (left) the raw spectra and (right) the processed spectra obtained.

Use of Orange

Orange is not often employed in the manuscript, being generally restricted to dots that embellish the vibrant blue, or for outlining roundels. One vibrant orange dot that overlays the vibrant blue was examined by Raman spectroscopy and found to be red lead. As shown in Figure 68, the Raman peaks at 120 and 536 cm^{-1} are barely visible in the raw spectrum but are revealed in the processed spectrum. These peaks correspond with published data that note the peaks as being at 121 and 549 cm^{-1}.

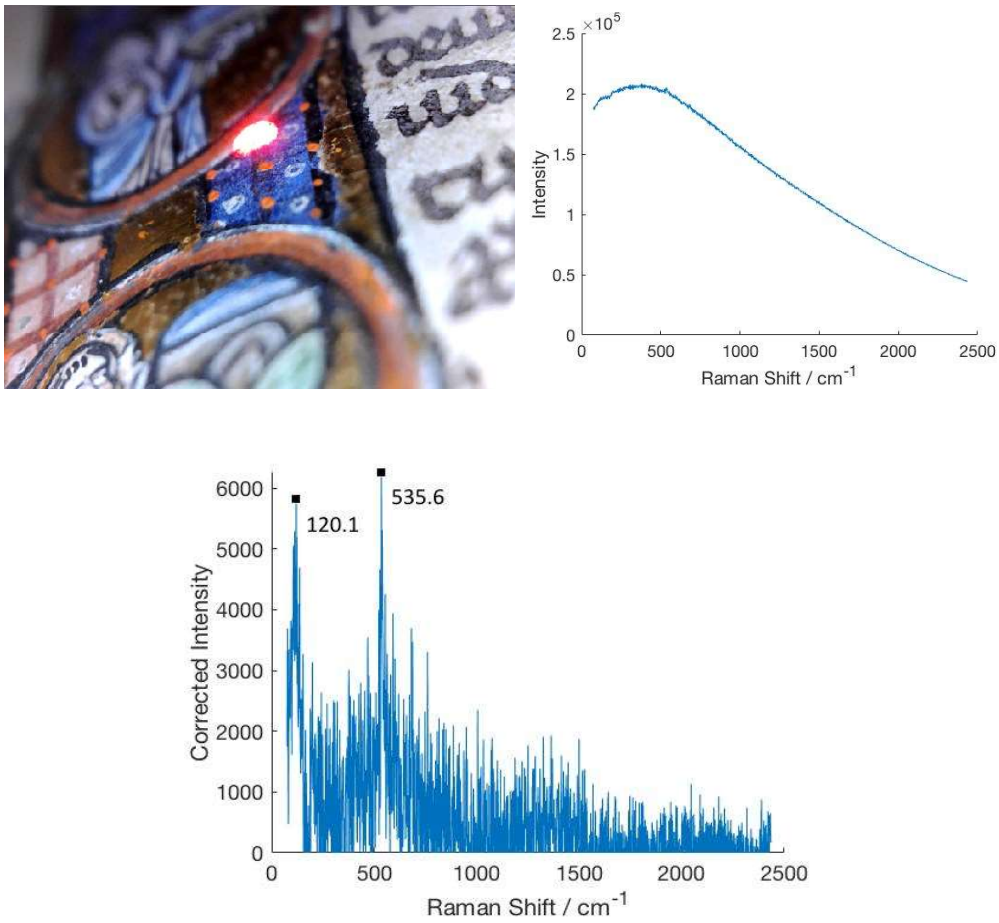


Figure 68: (top left) The area examined on A.IV.37 fol. 5r, (top right) the raw spectrum obtained, and (below) the processed spectrum.

An orange-brown was also examined with the Raman spectrometer, and this too was found to be red lead, as seen in Figure 69. Again, the peaks at 120 and 549 cm^{-1} are difficult to ascertain in the raw spectrum but can be seen in the processed spectrum. These peaks (which tally with those in published data as described above) identify the colourant as containing red lead, despite their hue being browner than one would normally associate with red lead, probably due to red lead degradation. The degradation could be due to the nature of the binder and/or could be due to the application of the paint being quite thin in this area, meaning geater exposure to the air.

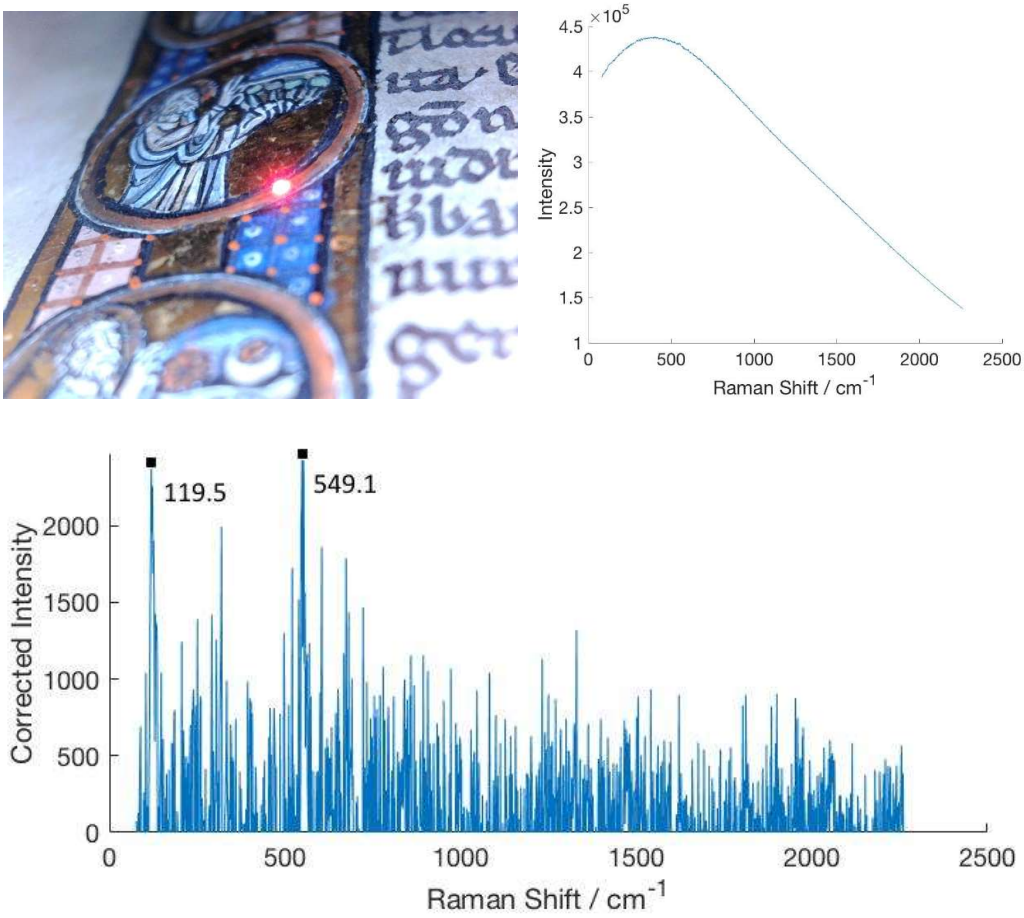


Figure 69: (top) The area on A.IV.37 fol. 5r that was examined, (left) the raw spectrum obtained, and (right) the processed spectrum.

Use of Green

Figure 70: Photomicrographs from two sections of the initial on fol. 5r. Each circle is approximately 1 cm in diameter.

Green was reserved for contexts wherein the pictorial subject matter mandated it (see Figure 70 above); it was never used for decorative details or purely aesthetic effect. It is difficult to tell, even when looking through a microscope, if the two tones of green are deliberate or a result of the drying of paint. The darker green on fol. 5 was examined, and the results are shown in Figure 71 below.

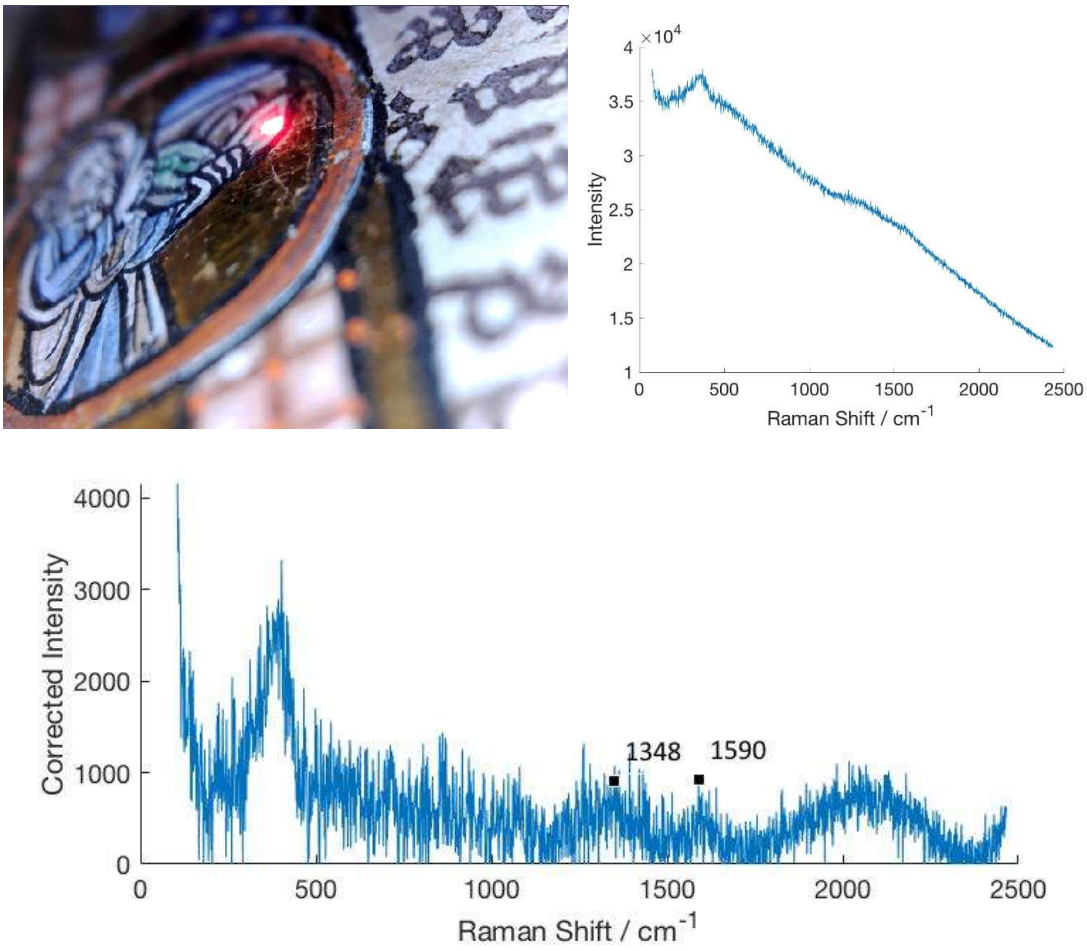


Figure 71: (top left) The area of A.IV.37 fol. 5r examined, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

Ignoring the artefact of the system that results in a peak centring on 400 cm^{-1}, there are peaks at 1348 and 1590 cm^{-1} which suggest that carbon is present, consistent with the peaks in published literature for carbon at 1346 and 1582 cm^{-1}. The presence of carbon in a green paint is unusual, and could potentially be explained as an anomaly - the laser has detected errant traces of carbon. However, as the green is the darker of the two green seen, it could be that the carbon is a deliberate addition to darken the colour.

To verify the presence of carbon, another patch of green was analysed in a different area of the initial, and the spectrum obtained is shown in Figure 72 below. Again, carbon was detected with peaks at 1344 and 1585 cm^{-1}. In addition, white lead was also detected, with a clear peak at 1057 cm^{-1} and another peak at 148 cm^{-1}. The nature of the processing has almost removed the 148 cm^{-1} peak from the processed spectrum, despite being very clear in the raw spectrum.

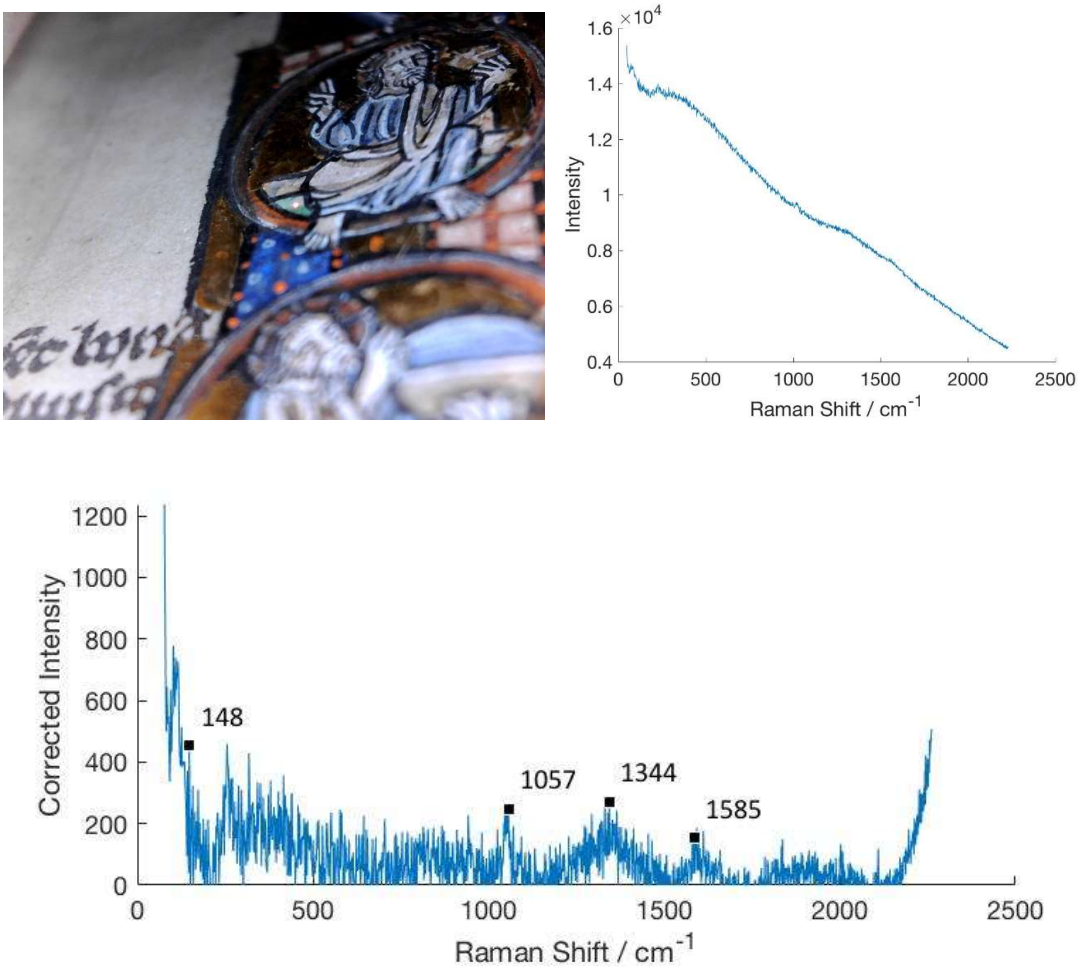


Figure 72: (top left) The area of A.IV.37 fol. 5r examined (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

The fact that carbon is detected again, and white lead too, suggests that the green is a mixture of colours that includes both these pigments, probably to vary the shade. Clearly, the paint must contain a pigment whose colour is green - likely copper-based. The inclusion of white lead could be as a substrate or to lighten the colour, whilst carbon may have been used to darken the colour. However, the presence of so many black outlines, which are likely to be carbon, cannot rule out that the presence of carbon seen here is contamination.

The green area of pigment in the damaged area of fol. 5r was also examined by FORS, with the resulting spectrum shown in Figure 73 (the damaged section of the initial can be seen previously in Figure 58 and Figure 59 above). Here the spectrum reveals an absorbance maximum of 690 nm,

consistent with that for copper resinate at 695 nm.[49] However, the area is so damaged, that whilst the pigment is likely to be copper-based, further investigation would be needed to say that the pigment was definitively copper resinate.

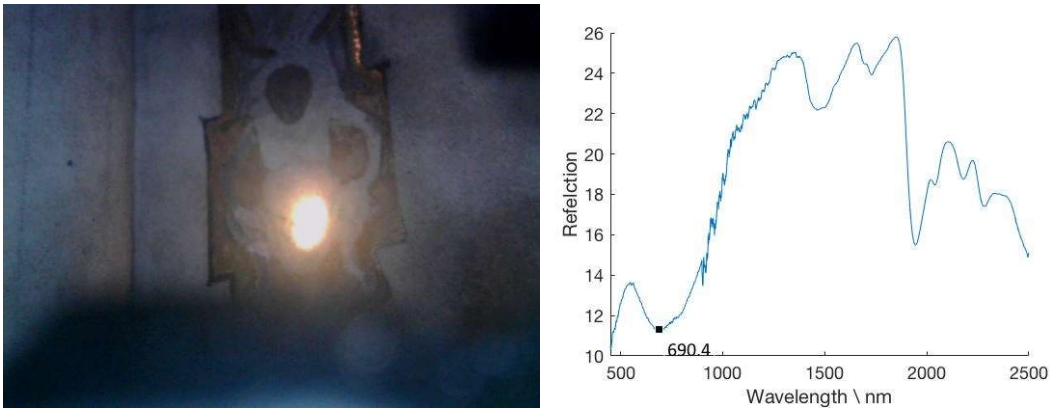


Figure 73: (left) The exact area on DUL A.IV.37 fol. 5r that was examined by FORS, and (right) the resulting spectrum.

Use of black

As mentioned above, black is used frequently in the manuscript as it outlines most of the drawings and initials. A thick black outline to the initial on fol. 5 was examined with Raman spectroscopy, as shown in Figure 74. The processed spectrum reveals two peaks that are just visible in the raw spectrum, at 1326 and 1592 cm^{-1}. These peaks are those of carbon black, as published in library data, at 1349 and 1597 cm^{-1}.[50]

As discussed in Chapter Two, the use of carbon for black was ubiquitous in medieval manuscript manufacture, due to it being cheap, quick and easy to make. Its use here seems clear, although had the line been thicker an examination by FORS would have confirmed this - if the pigment were indeed carbon, it would have produced a characteristic spectrum - one with very little refection at all, i.e., a flat line, in the visible region of the spectrum.

[49] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.
[50] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts'.

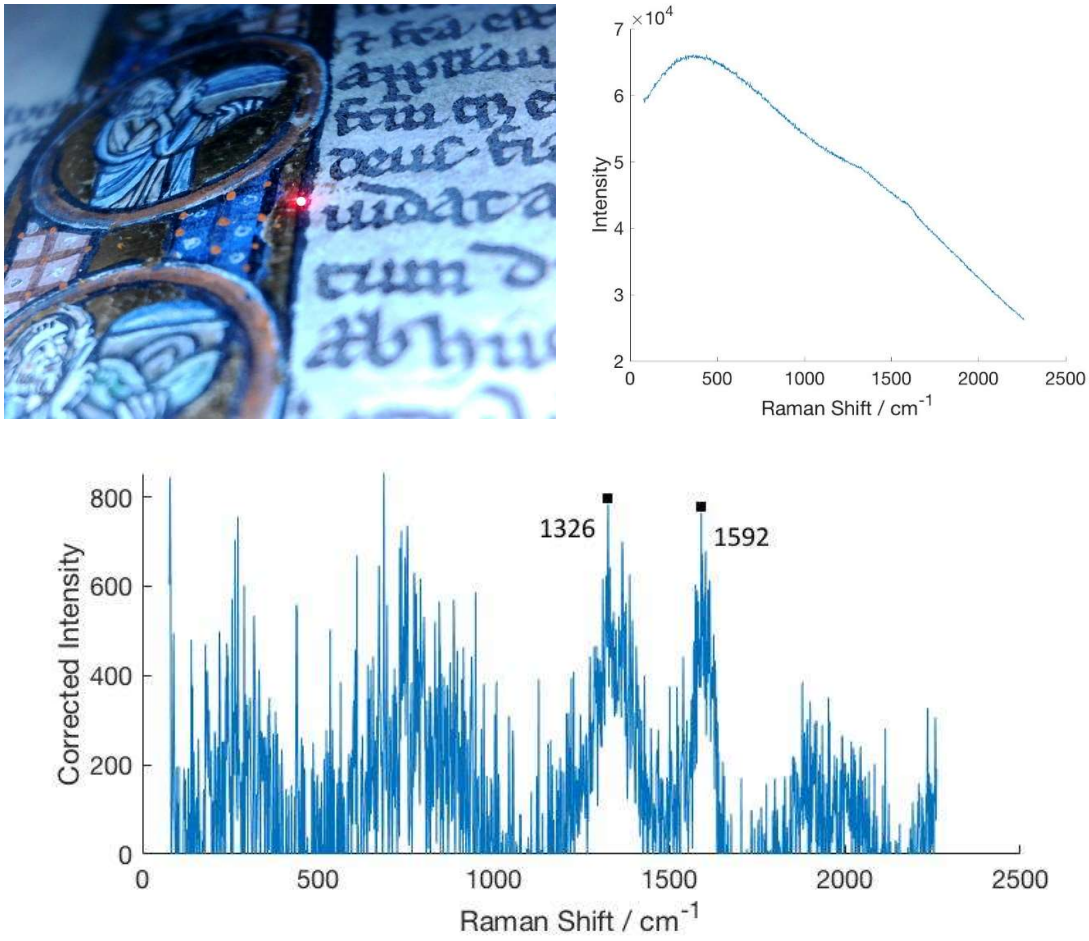


Figure 74: (top left) The outline to the initial examined, (right) the raw spectrum obtained, and (bottom) the processed spectrum obtained.

Use of pink

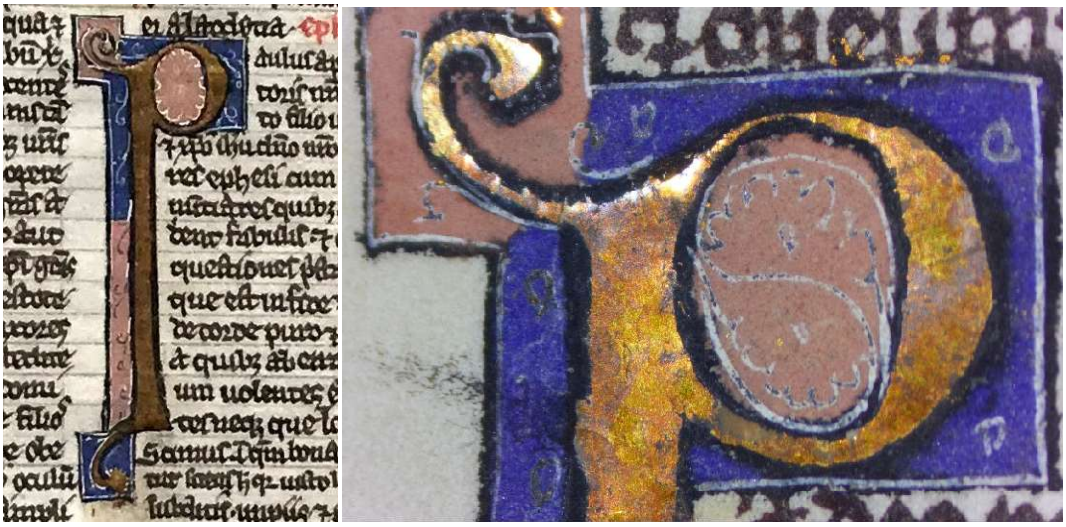


Figure 75: (left) The initial 'P' on A.IV.37 fol. 337r in full, and (right) a close up of the pink and blue surrounding the bowl of the letter P.

The pink used in A.IV.37 provides a pleasing visual contrast to the vibrant blue and is therefore often found alongside it, as seen in the initial on fol. 337r in Figure 75 above. As mentioned previously, pink paint in manuscript art is often a mixture of colourants, and often contains organic dyestuffs, making identification difficult.

The pink in the initial on fol. 337r was examined by Raman spectroscopy and did not return a spectrum with any identifiable features, as seen in Figure 76 below.

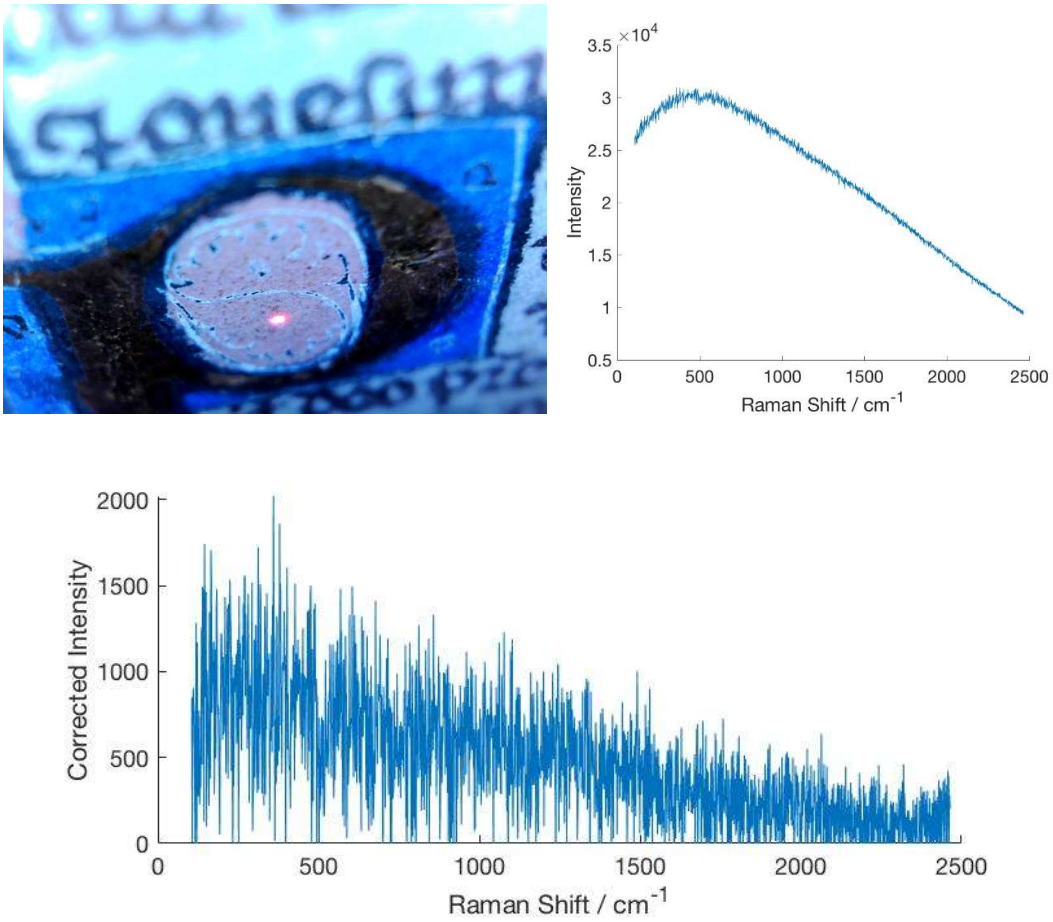


Figure 76: (top left) The spot on A.IV.37 fol. 337r where the pink infill was examined, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

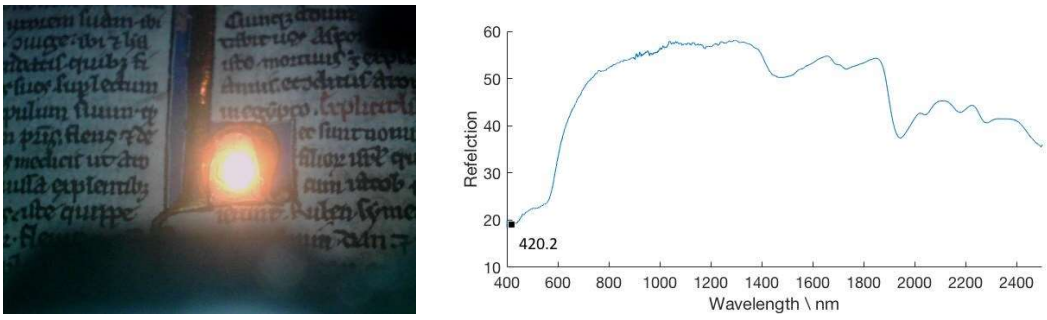


Figure 77: (left) The area on DUL A.IV.37 fol. 18r examined by FORS, and (right) the resulting FORS spectrum.

The pink in the initial on fol. 18 was examined by FORS, and the results can be seen in Figure 77. The absorbance maximum at 420 nm is curious, as in published data this point corresponds more to organic yellows such as weld, turmeric, or stil-de-grain. Although it is certainly possible that an organic

pink had organic yellow components, it is unlikely in this case that this absorbance maximum is revealing any pertinent information.

Use of white

White is used frequently in the manuscript for hands and faces of figures in historiated initials and for clothes and draperyIt is also used to provide detail and embellishment to plain blocks of infill (seen in Figure 68 and Figure 75, for example).

A white area on fol. 5r was examined with Raman spectroscopy, and the resulting spectrum is shown below in Figure 78. The raw spectrum shows peaks at 113 and 1052 cm^{-1}, which correspond with published data for the peaks in white lead, reported at 104 and 1050 cm^{-1}. The processed spectrum is not included here, as it does not highlight the white lead peaks.

As discussed above, a FORS spectrum of the white paint was not obtained from this manuscript. To confirm the paint as containing white lead, a FORS spectrum with an absorption band at 1447 nm would be expected.[51]

[51] Delaney et al., 'Use of Imaging Spectroscopy, Fiber Optic Reflectance Spectroscopy, and X-Ray Fluorescence to Map and Identify Pigments in Illuminated Manuscripts'.

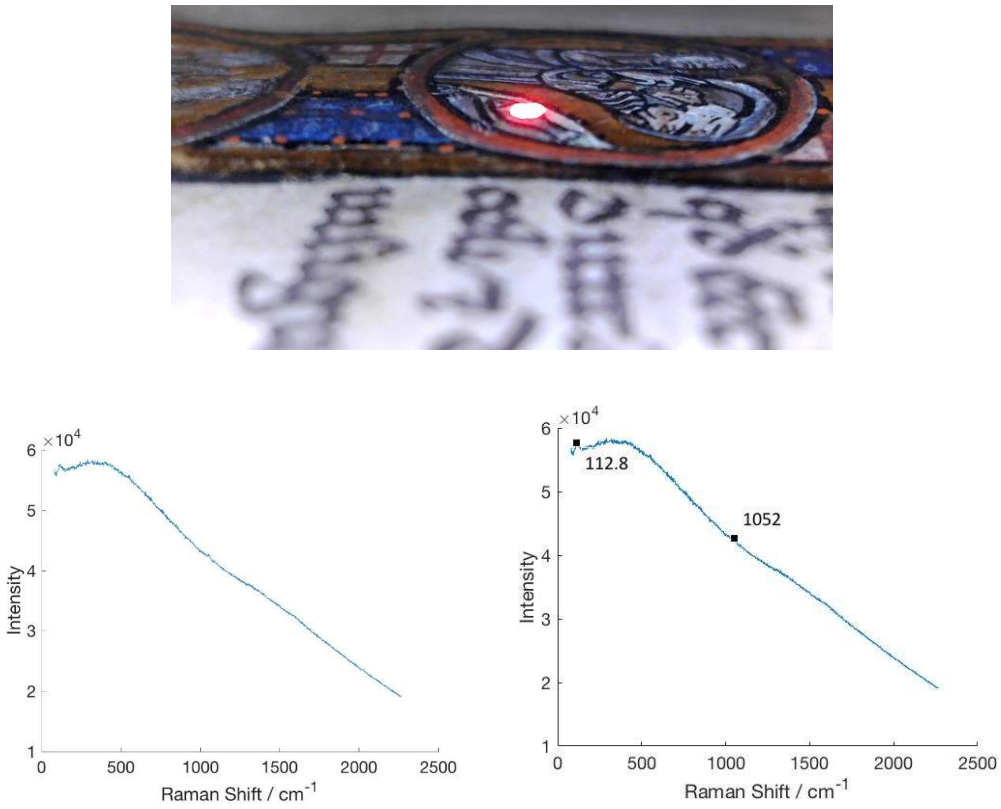


Figure 78: (top) The area on fol. 5r examined, (bottom left) the raw Raman spectrum obtained and (bottom right) the labelled raw spectrum, indicating white lead.

Use of gold

As demonstrated by the two initials in Figure 79, gold was used in the manuscript either to fill the initial as on fol. 337r, or to infill behind artwork in the initial, as on fol. 5v. As described more fully in Chapter Four Part A, there is little value in examining gold with Raman spectroscopy or FORS. In this instance, the photomicrographs show the gleam and lustre of the metal, which looks to have been applied in leaf and then burnished. XRF (explained in Chapter Three) would be able to ascertain the purity of the gold and tell if the metal was an alloy.

Figure 79: (left) Part of the initial on fol. 5v and, (right) part of the initial on fol. 337r showing use of gold.

Text and text ornamentation

The blue and red display script capitals of the running heading on fol. 5r were examined with Raman spectroscopy and with FORS and were found to contain lapis lazuli and vermilion. As we have seen in the other manuscripts examined thus far in the project, these are usual pigments used for this type of text feature. That the blue is pure lapis lazuli and contains no azurite is interesting but not unusual and suggests that no expense was spared in the choice of the use of blue.[52]

The lapis lazuli peaks at 554 and 1098 cm^{-1}, shown in Figure 80 below, correspond with those given in published data - at 545 and 1096 cm^{-1}.

[52] Richard Gameson et al., 'Late Medieval English Illuminators' Blues', (forthcoming).

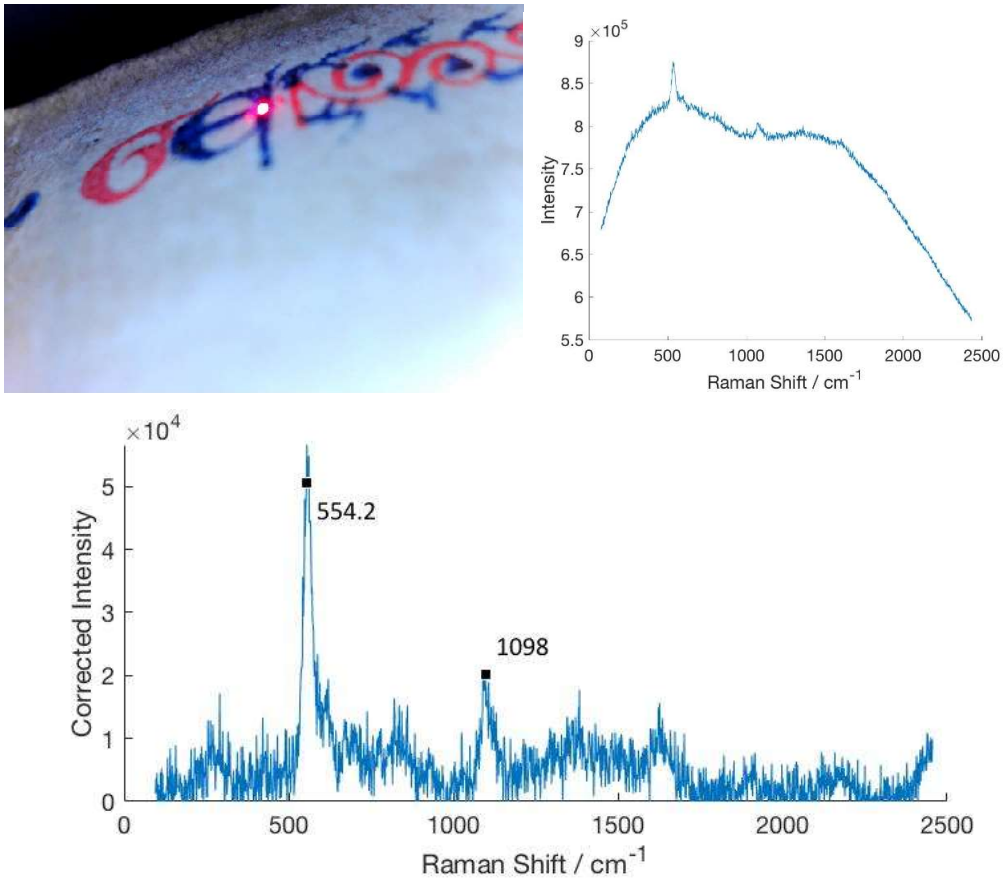


Figure 80: (top left) The spot examined on fol. 5r, (top right) the raw Raman spectrum obtained, and (bottom) the processed spectrum.

The FORS spectrum, from a display script capital on the same page, shows an absorbance maximum of 619 nm, consistent with that of lapis lazuli given in published sources. In addition, there are no absorbance bands present at 2285 and 2352 nm, meaning that azurite is not present in the area examined.

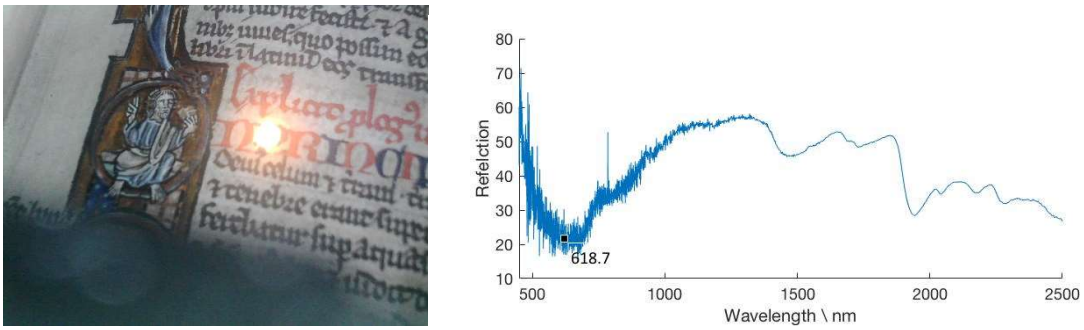


Figure 81: (left) The area of A.IV.37 fol. 5r examined, and (right) the FORS spectrum obtained.

The vermilion peaks, shown in Figure 82 below, at 249 and 337 cm^{-1} are consistent with those given in published data which report them as being at 251 and 342 cm^{-1}.[53]

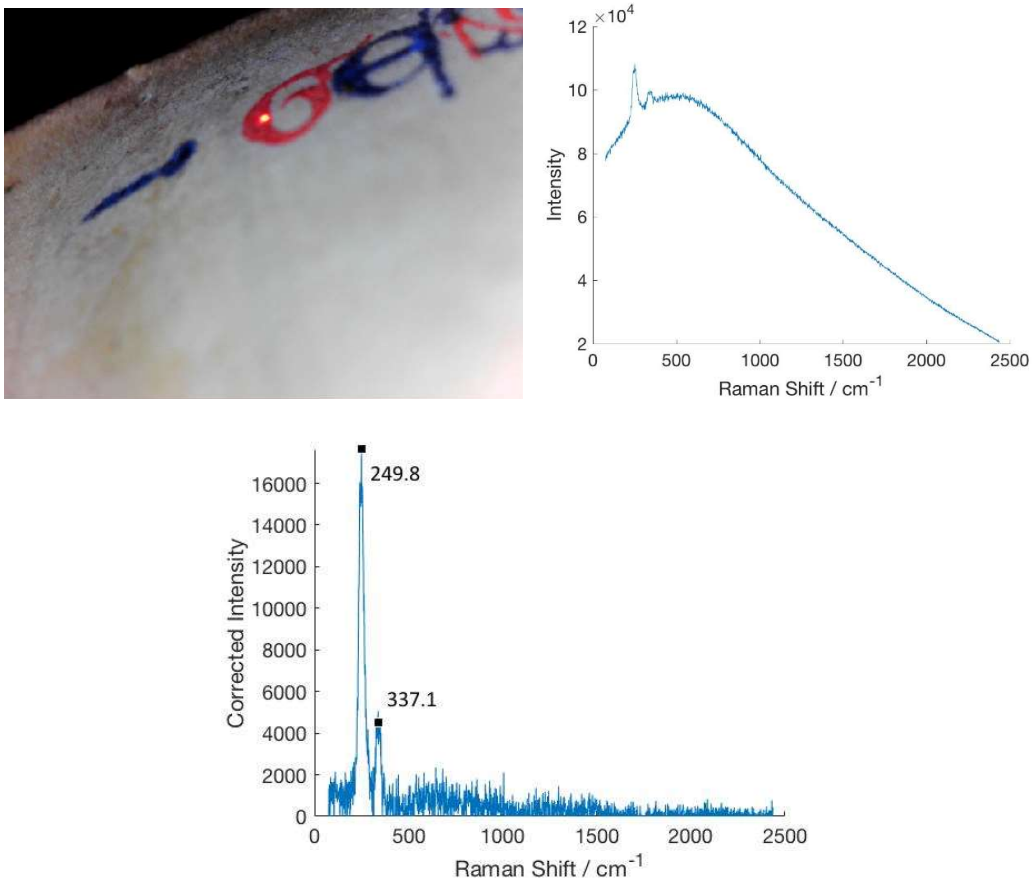


Figure 82: (top left) The spot on A.IV.37 examined by Raman spectroscopy, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

[53] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', page 1222.

The FORS spectrum, from the red display script on the same page, is shown in Figure 83. Here the inflection point of 602 nm is in accordance with that given in published data for vermilion, which states that the inflection point is 600 nm.

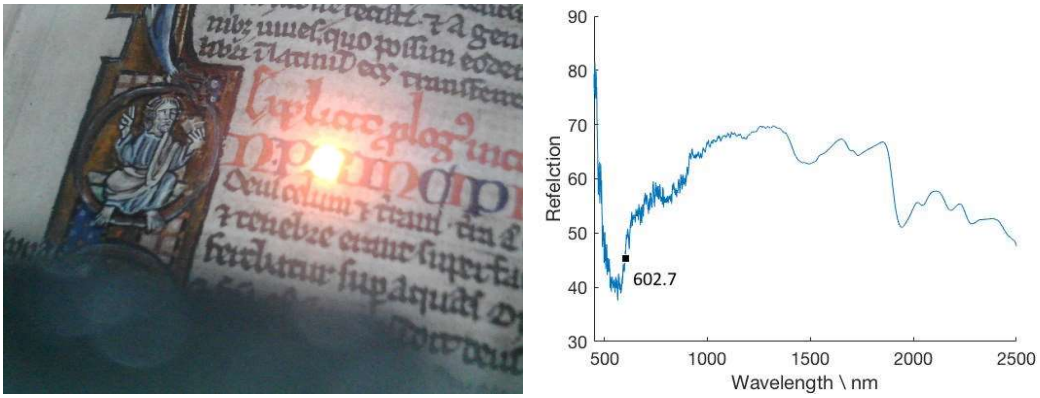


Figure 83: (left) The area on A.IV.37 fol. 5 examined with the FORS system, and (right) the spectrum recorded.

Text

The black text seen in many images so far in this section was examined with Raman spectroscopy, as demonstrated below in Figure 84. Despite published literature recording that oak gall ink has a broad peak at 1573 cm^{-1}, this was not seen under the low laser power used in the examination of this manuscript.[54] The raw spectrum could be considered to have a very broad peak at around 1570 cm^{-1}, although this does not appear in the processed spectrum. Nevertheless, as there was no indication that carbon (the alternative black pigment) was present and given that gallotannic formulations were used for the overwhelming majority of inks at this date, it is likely that such was the case here too.

[54] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

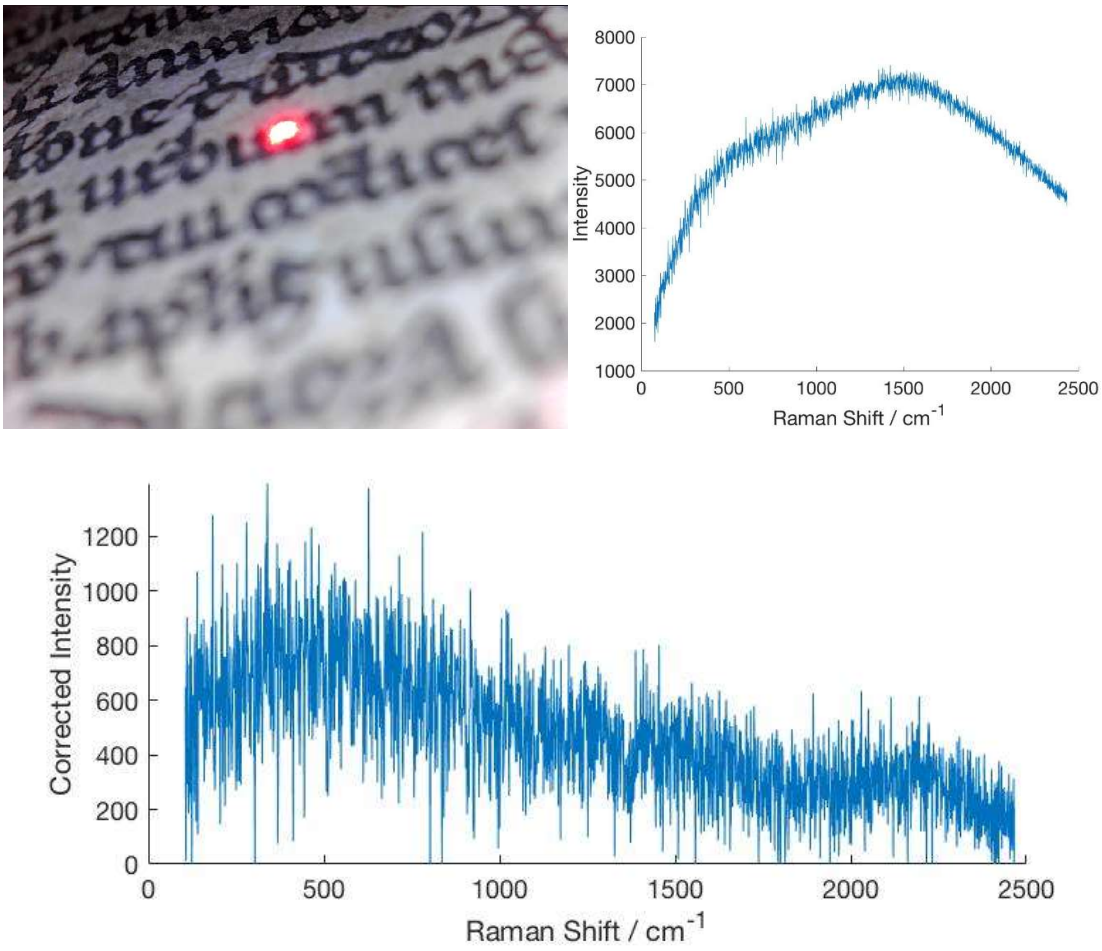


Figure 84: (top left) The spot on fol. 5r where the ink was examined, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

Rubric

The orange rubric on fol. 5r was examined and found to be vermilion, which is not unusual, as seen in Figure 85 below. Although it was more common for red lead to be used to provide an orange colour, vermilion too can be processed to create a range of hues - from vivid blood red to the orange we see in this case. In the spectrum, the peaks seen at 259 and 351 cm^{-1} correspond to those in published data (at 251 and 342 cm^{-1}).[55]

[55] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts' p. 1222.

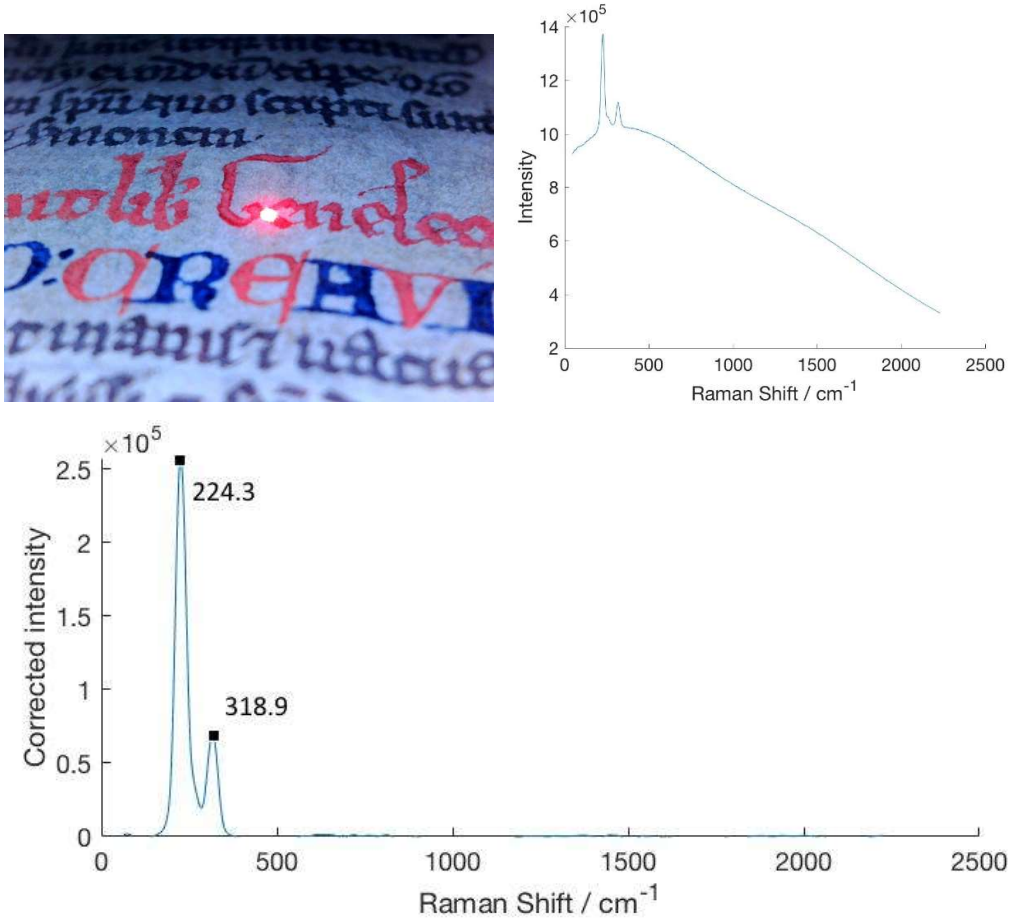


Figure 85: (top left) The area on fol. 5r examined, (top right) the raw spectrum obtained and, (bottom) the processed spectrum.

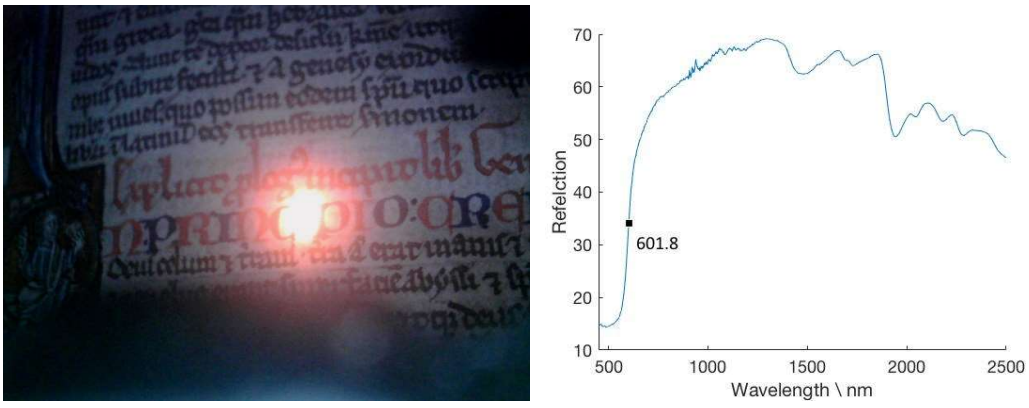


Figure 86: (left) The spot on the red display script on DUL A.IV.37 fol. 5r that was examined by FORS, and (right) the resulting spectrum obtained.

The red display script on fol. 5r was examined by FORS and found to be vermilion, as shown by the spectrum in Figure 86. The inflection point in the spectrum is at 602 nm, consistent with that in published data, at 600 nm.[56]

Further comments on the palette as a whole

The pigments used to create the palette used are in keeping with the time and place of its creation. Lapis lazuli, vermilion, red lead, white lead and carbon are certainly used, alongside a likely organic-based mixture to create a dusky pink, and a concoction of white lead, carbon and a green copper-based pigment to make two shades of green. Gold is used extensively. The ink contains no carbon and is probably gallotanic.

In contrast to the economy that seems to have resulted in the use of mediocre parchment and the multiple (sometimes enormous) copying errors, the artwork, whilst limited, seems to tell a different story. As revealed by the photomicrographs, much care and attention was lavished on the painting, with both careful evocations and detailed use of paint. The use of different shades of colours, especially in the blue drapery, reveals skilled colour mixing and application. This high-quality artistry is combined with a considered palette. The use of lapis lazuli, rather than the cheaper azurite, for all the blues - even those of the text initials and running headings - indicates that cost was not an issue. Furthermore, the extensive use of gold supports this notion.

[56] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

Chapter Four Part C

Analysis of NCO MS 1 and NCO MS 20

Colour Analysis of Pink and Blue

Conclusion of All Analyses and Broader Context

New College Oxford Manuscript 1

Notes

New College Manuscripts MS 1 and MS 20 were examined *in situ* at New College Library, Oxford, in late February 2020. Our work imposes upon our hosts, requiring the use of a room with suitable space that can be made completely dark. Furthermore, it is usual to have a member of staff from the host institution present at all times. Naturally, these factors limit the time available to examine manuscripts, and so the data collected here is that which could be obtained during the few hours available.

Figure 1: An initial in The Book of Job, NCO MS 1 (folio not recorded).

Description and provenance

NCO MS 1 is a thirteenth-century Paris Bible. The provenance of the manuscript is undocumented prior to its donation to New College by the founder, William of Wykeham; an inscription suggests that it had a period in the keeping of John Penyton, a fellow of the college from 1495-1519.[1]

Codicology

Text layout and ornamentation

Figure 2 below shows the typical layout of the book, with the text in two columns of 55 lines. A decorated initial and red and blue display scripts head each book. Red and blue are deployed for running headings across an opening, and the same colours are used for chapter numbers. Rubrication is red, whilst the text is black.

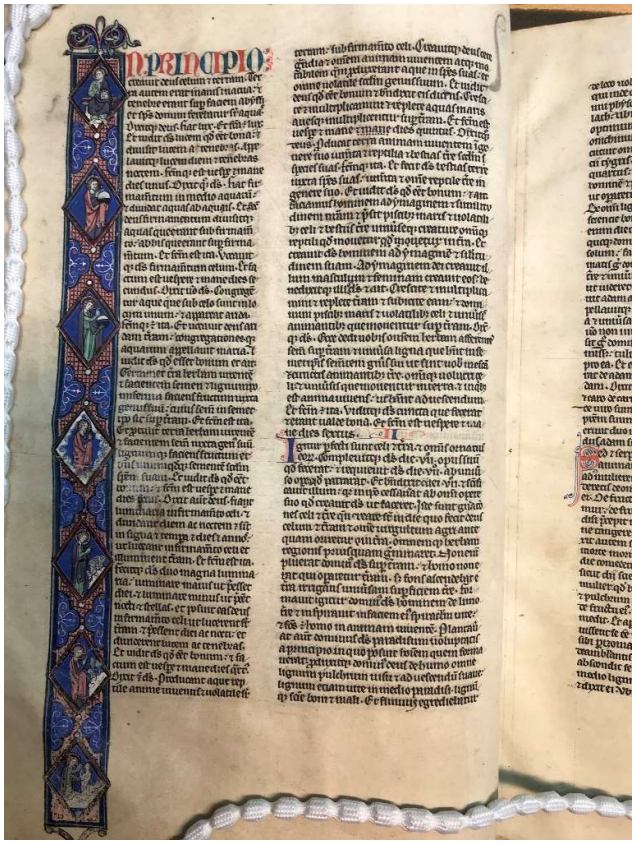


Figure 2: NCO MS 1 fol. 3v.

[1] Henry Octavius Coxe, *Catalogus codicum mss. qui in collegiis aulisque oxoniensibus hodie adservantur* (Oxonii : e Typographeo academico, 1852); Bodleian Library, 'MLGB3 Home', accessed 28 April 2020, http://mlgb3.bodleian.ox.ac.uk/.

Script and hands

The black script is a neat Textualis quadrata, evidenced by the fact that the minims invariably terminate in a diamond shape despite the small size of the text, seen clearly in Figure 3 below. This script is indicative of a high-grade manuscript.

Figure 3: A close-up of the script on fol. 1r.

Artwork

Style of artwork

Similar to other books examined in this study, the manuscript contains many historiated initials with plain coloured backgrounds. Although stylised, the figures are deftly painted, especially the clothes, which contain intricate folds and shadows, as can be seen below in Figure 4. The faces, hands and hair are brief but confidently articulated with thin lines and, as Figure 4 shows, contain delicate shading and contouring to detail the face. The neat artwork and skilled application of paint give the impression that this is a high-grade manuscript. The style is one associated with the middle or second half of the century.

Overview

Like NCO MS 20 and other manuscripts seen so far in this study, blue and pink characterise the palette. As seen in the initial in Figure 1 above and Figure 4 below, blue is in both the ground of the initial, as well as in the drawing where it colours the clothing. A contrasting dusky pink, in various shades, is similarly deployed in the ground and in the initial itself. Both colours are echoed in the flourishing.

Figure 4: An initial from Job in NCO MS 20 (fol. not recorded).

Aside from pink and the vibrant blue, a blue-grey is also employed. It is used regularly for clothes but is not seen as infill or in the ground of initials. Again, as seen in NCO MS 20, a vibrant orange is deployed sparingly for small objects and to add detail (see Figure 4 above, where both the book and Job's cheek are coloured orange). Similarly, a vibrant green is seen in small quantities. White and black are employed in their characteristic ways – white to highlight, add detail to the decoration, and for flesh, and black to outline the drawings and decorations and to colour small objects. The text is black, and bright red and blue are used for text ornamentation, with red also used for rubrication.

Unlike the manuscripts encountered hitherto, NCO MS 1 displays two purple colourstuffs. Best seen in the photomicrograph in Figure 5 below, one purple colours the column head decoration, and the other shades the grey clothing on the left of the picture.

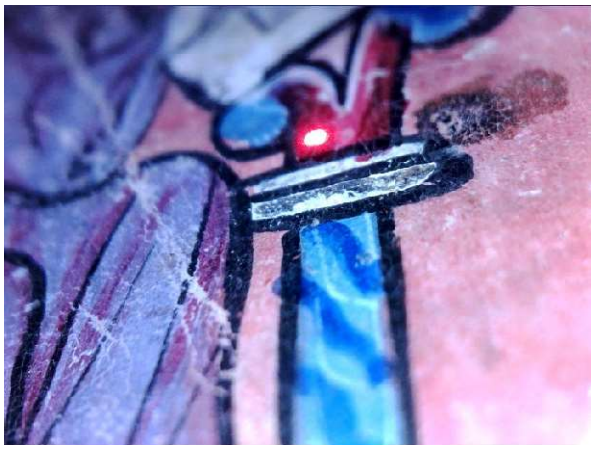


Figure 5: A photomicrograph showing the use of pink, the purple in the column heading, and the other purple shading the clothing. (NCO MS 1, fol. 1 r)

Use of Blue

As mentioned above, much use is made of blue through the manuscript. In Figure 6 below, the initial on fol. 1r shows blue colouring the initial itself as well as parts of the drawing. Although it can be hard to discern by eye when looking at an image, the outside of the initial is a slightly different colour blue from the inside of the initial.

Figure 6: The initial on NCO MS 1 fol. 1r.

Figure 7 below illustrates that, when examined with Raman spectroscopy, the outside blue was found to contain lapis lazuli as the peaks returned at 551, 1094 and 1657 cm^{-1} correspond to those given for lapis lazuli in published data (at 545, 1096 and 1662 cm^{-1}). [2]

[2] G. Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', *Analytical Methods* 10, no. 10 (2018), p.1222.

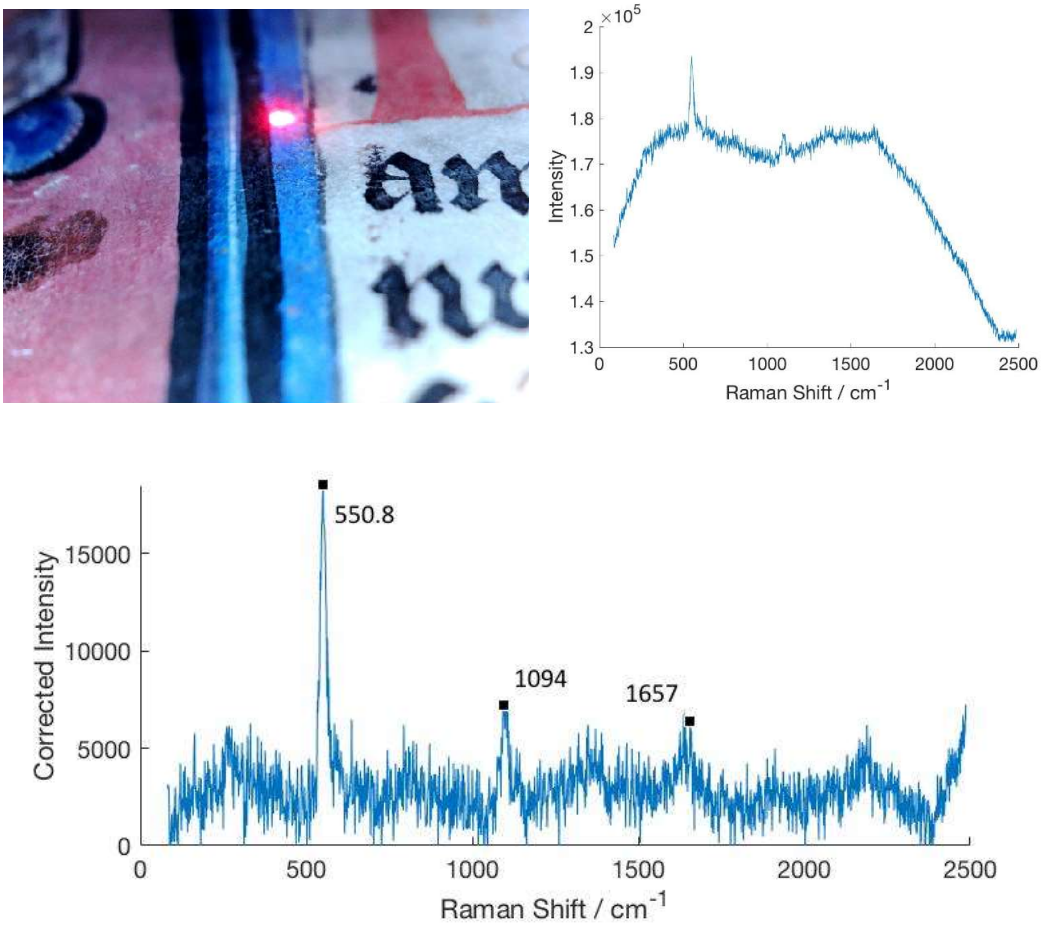


Figure 7: (top left) Area of blue in initial of NCO MS 1, fol. 1 r examined, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

The blue colour on the inside of the initial did not return a Raman spectrum of lapis lazuli, however. This area was examined by FORS and found to be azurite, with the spectrum recorded seen in Figure 8 below. The absorbance maximum of 639 nm is almost exactly that given for azurite in published literature (640 nm) and the absorbance bands at 2285 and 2354 nm also correspond with that in published data (where they are given as 2285 and 2352 nm).[3]

[3] Maurizio Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', *Analytical Methods* 6, no. 5 (2014), p. 1491; R. Mulholland et al., 'Identifying Eighteenth Century Pigments at the Bodleian Library Using in Situ Raman Spectroscopy, XRF and Hyperspectral Imaging', *Heritage Science* 5, no. 1 (18 October 2017), p. 11.

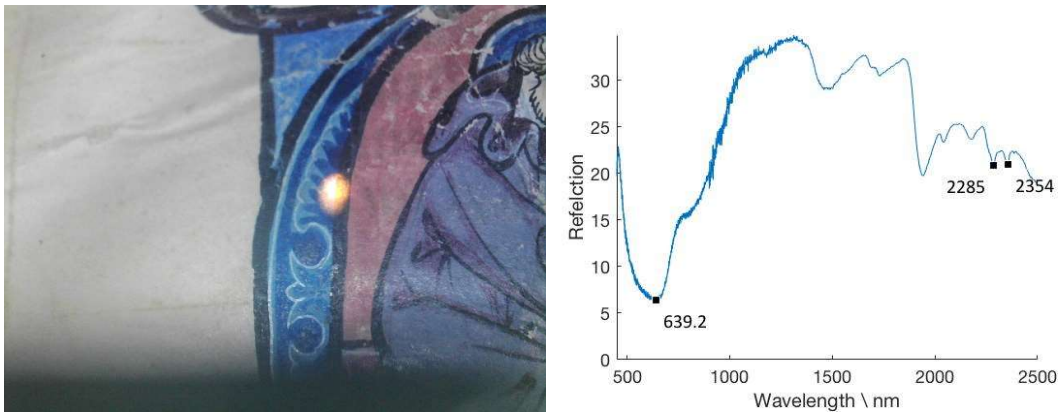


Figure 8: (left) The spot on fol. 1r examined, and (right) the spectrum obtained.

As can be seen in Figure 9 below, the areas which contain lapis lazuli and azurite can easily be distinguished. Under infrared illumination, the azurite blue pigment, employed for the initial itself, for the bench, and the writing apparatus in the illustration (as well as the A in the display script to the right) are all dark. The blue infill outside the initial is light, indicating that this is lapis lazuli.

Figure 9: (left) A photomicrograph of the initial on NCO MS 1, and (right) the same initial under infrared illumination.

A darker blue on fol. 401r was also examined by Raman spectroscopy, as evidenced in Figure 11, and was found to contain lapis lazuli, with peaks at 551, 1094 and 1657 cm^{-1}. These are consistent with lapis lazuli peaks in published data.[4]

Figure 8 above contrasts with Figure 10 below, which shows a FORS spectrum with no azurite, obtained from the blue ground in part if the initial on fol. 3v.Here, the absorbance bands at 2285

[4] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

and 2352 nm are not present, and the absorbance maximum is 601 nm, almost exactly that given in published works for lapis lazuli, at 600 nm.[5]

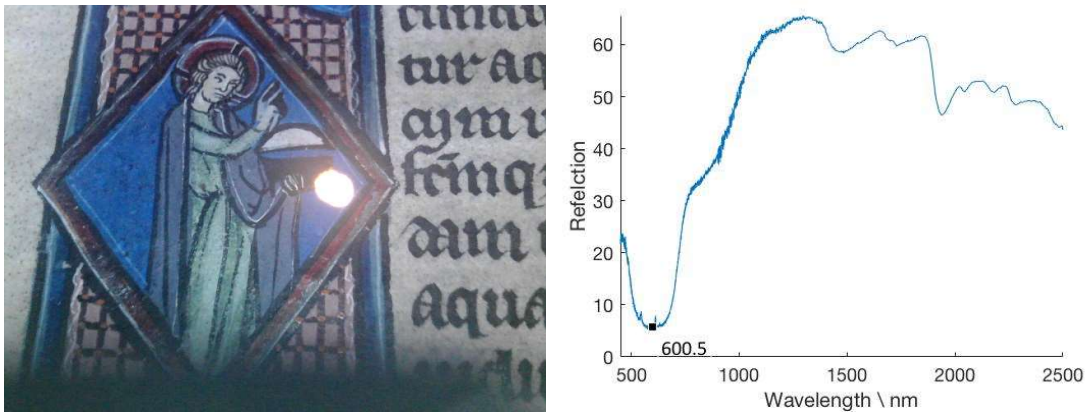


Figure 10: (left) The spot on fol. 3 v examined with FORS and (right) lapis blue ground.

[5] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p.1491.

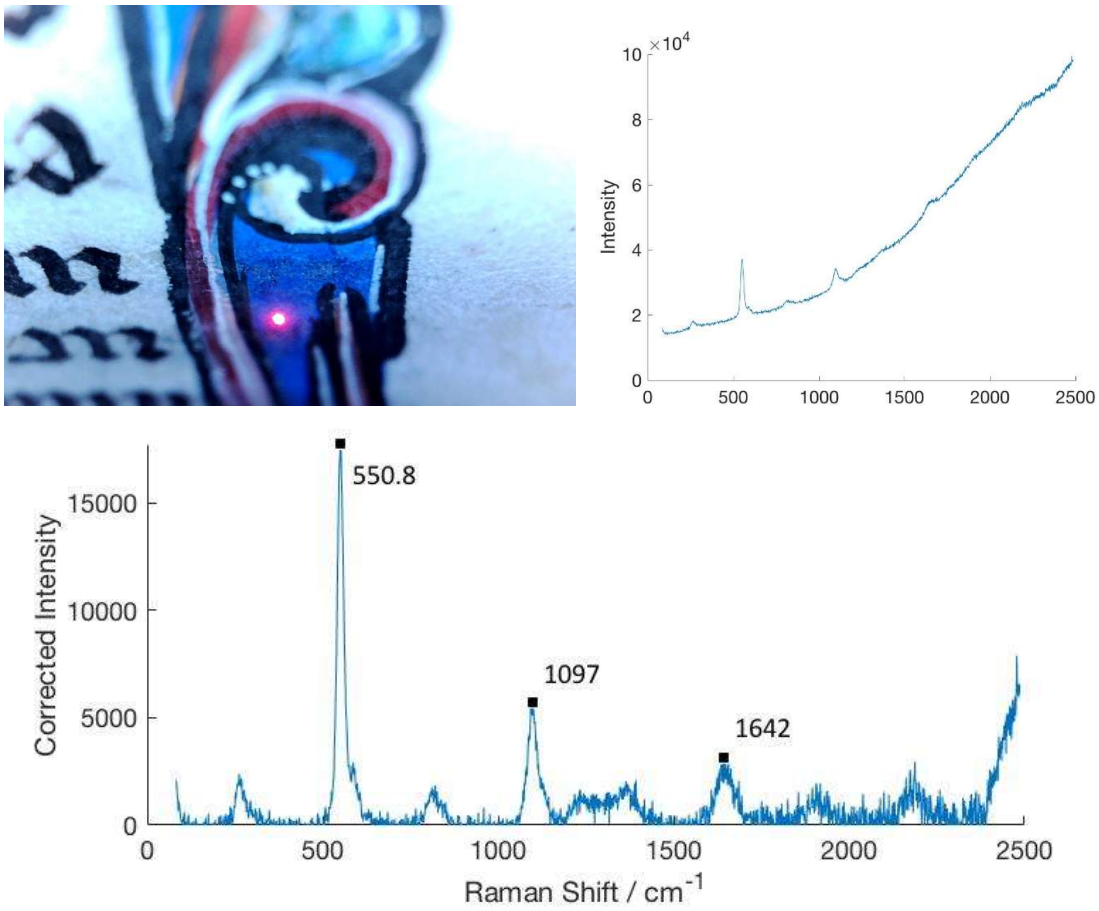


Figure 11: (top left) Area of blue in the initial of fol. 401 r examined, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

In sum, both lapis and azurite were used, deployed separately in different areas of the same initial. No mixtures were found. The difference in the hues of paint they produced - one lighter than the other - is typified by the inside and the outside of the initial on fol. 1, in Figure 8.This suggests that the deployment of both pigments in the same area was artistic preference (as opposed to economy or supply).[6]

[6] Richard Gameson et al., 'Late Medieval English Illuminators' Blues', (forthcoming).

Use of Grey

Figure 12: NCO MS 1 fol. 1v.

The grey colour could, on a different day or with a different eye, be placed in the section on the use of blue, as the colour of the grey sometimes verges on blue. Deployed principally for clothing, it is often shaded with a purple colour, discussed below, to accentuate the folds and draping cloth. Black lines of various thicknesses further indicate the grey folds.

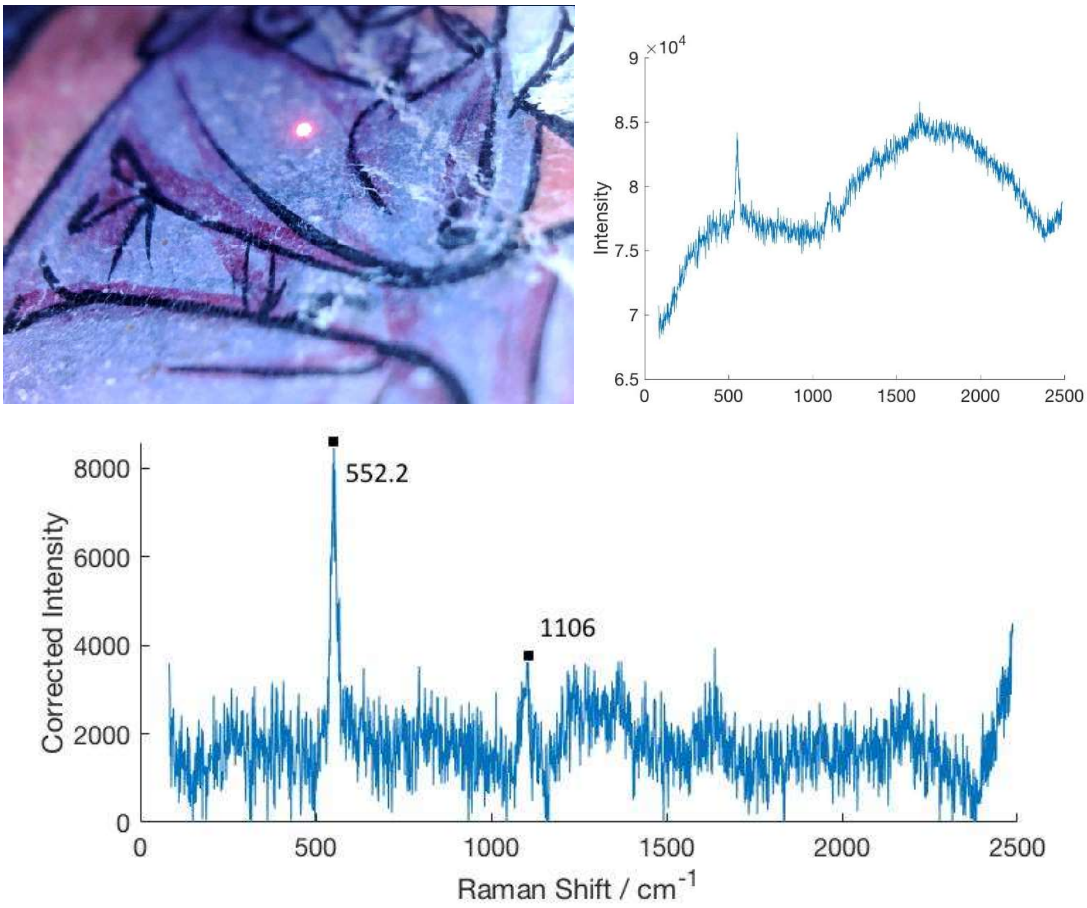


Figure 13: (left) Area of grey in the initial of fol. 1r examined (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

The grey cloak on fol. 1r was examined and, by the peaks in the spectrum at 552 and 1106 cm^{-1}, determined to be lapis ash. Lapis ash is confirmed by the presence of peaks at the same wavenumber as lapis lazuli (545 and 1096 cm^{-1} in published works).[7]

The grey on fol. 3v was examined with FORS and, as evidenced by the spectra in Figure 14, shows an absorbance maximum of 561 nm, not consistent with that for lapis lazuli in published works (600 nm) but not unexpected given that lapis ash is a different colour from lapis lazuli. The absorbance

[7] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

maximum at 600 nm is caused by the $S3^-$ chromophore.[8] With less of the chromophore colouring the lapis ash (as discussed in Chapter Two), the absorbance maximum will be altered.

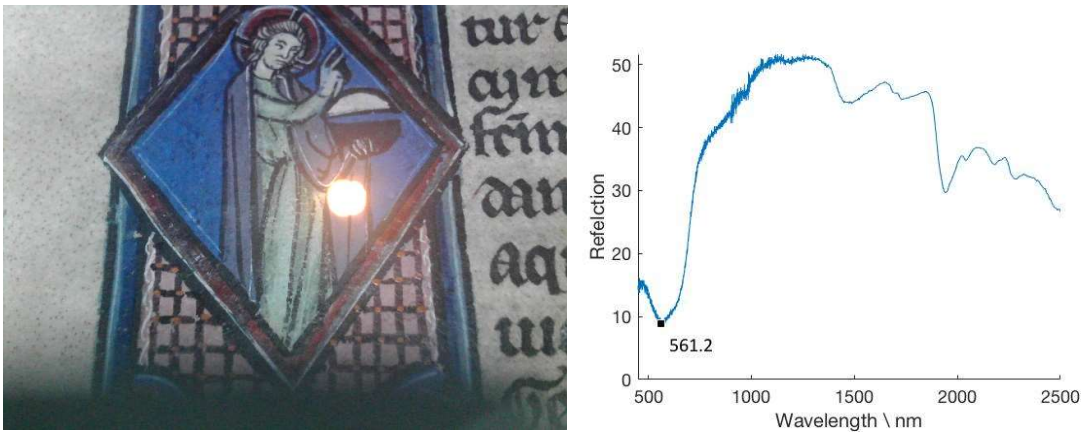


Figure 14: (left) The spot on the grey cloak in the initial on fol. 3 v examined by FORS, and (right) the resulting FORS spectrum.

Use of Orange

As seen below in Figure 15, a small orange decoration on fol. 401r was examined with Raman spectroscopy. Although the raw spectrum displayed considerable fluorescence, processing revealed a peak at 121 cm^{-1}, consistent with published data for red lead, which state that the peak is at 121 cm^{-1}.[9] No other peaks are discernible in either spectrum.

[8] Lain Wilson, 'The Techniques and Materials of the Wall Paintings at the Enkleistra of St. Neophytos (Phase II)', Page, Dumbarton Oaks, accessed 7 May 2020, https://www.doaks.org/research/byzantine/project-grants/kakoulli-fischer-2011-2012.

[9] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

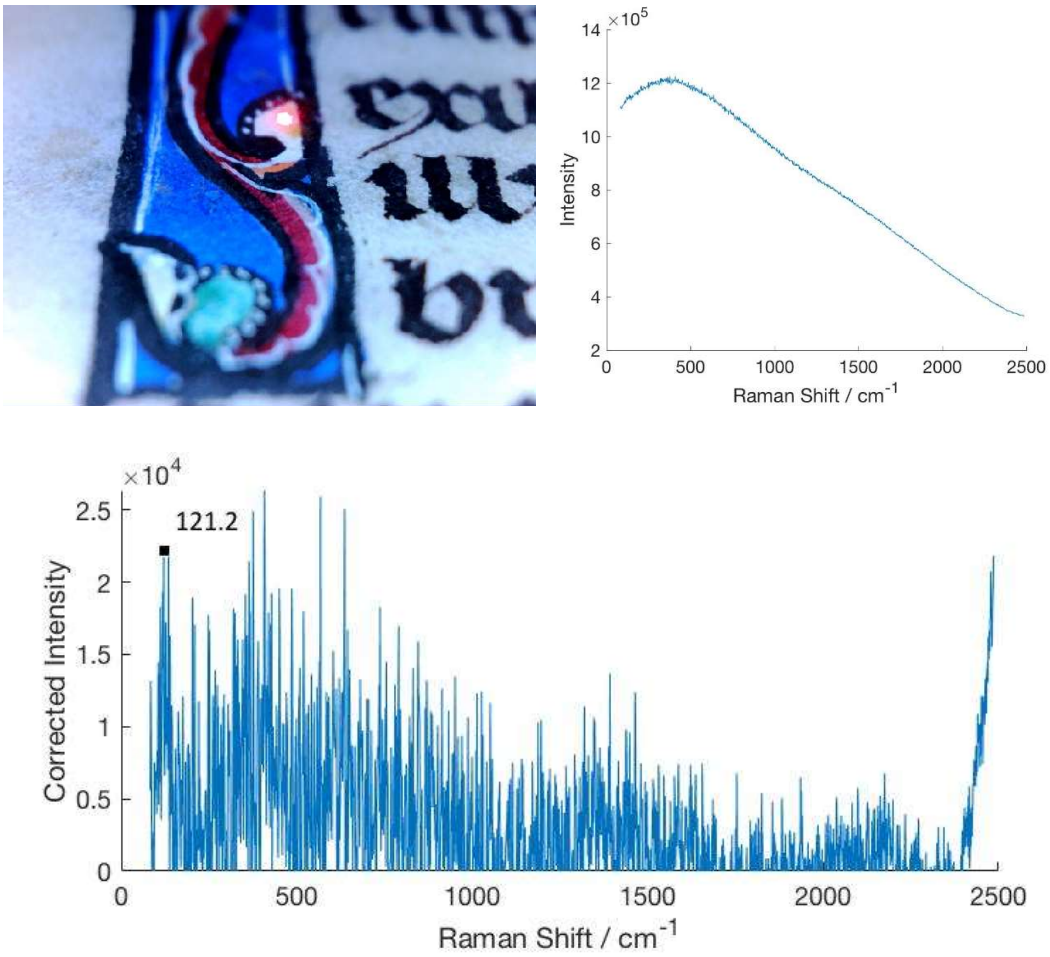


Figure 15: (top left) The orange spot on fol. 401 r examined with the Raman system, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

An orange area under the figure in the initial in fol. 401 was examined by FORS and is assigned as red lead due to the inflection point at 605 nm, as shown in Figure 16 below. The inflection point in published data is given as 600 nm.[10]

[10] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

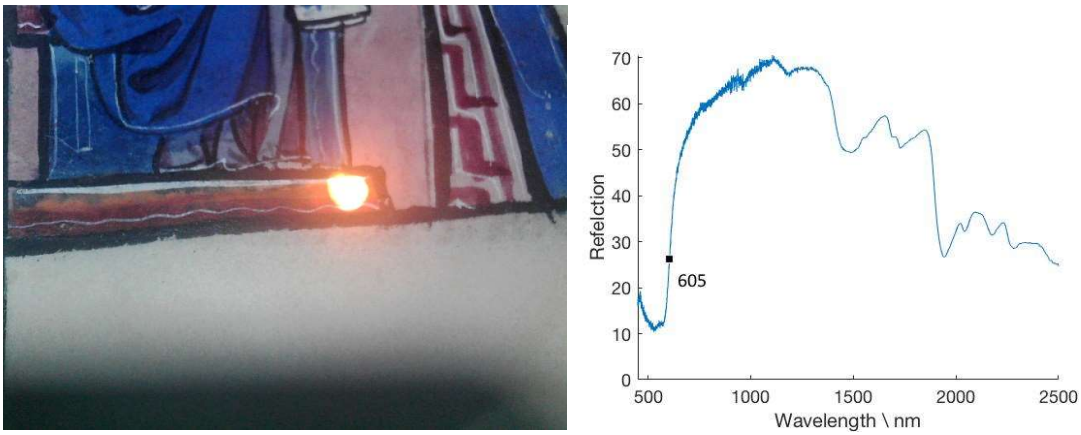


Figure 16: (left) The area of orange on fol. 401 r examined with FORS, and (right) the spectrum obtained.

Use of Green

Green, like orange, is used sparingly, as was noted above. The restraint with which it was applied can be appreciated from Figure 16.

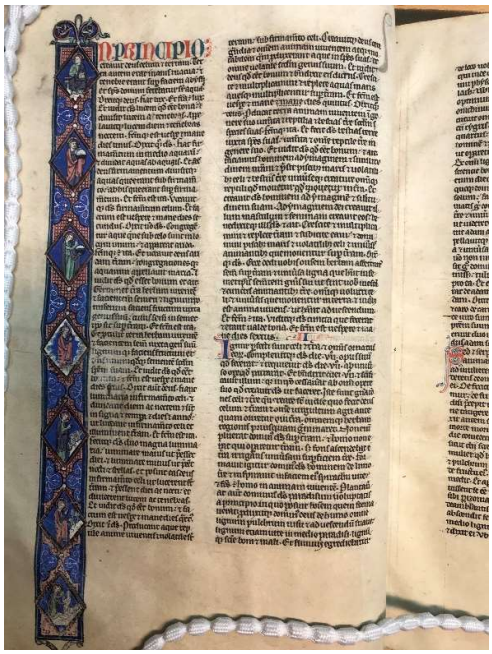


Figure 17: NCO MS 1 fol. 3v.

A green foliate curl on fol. 401r was examined with Raman spectroscopy, and the resulting spectra are shown in Figure 18 below. As can be seen in the raw spectrum, the intensity of the light received by the spectrometer is low compared to other spectra (see Figure 15 above, for example). This would suggest that the green pigment is absorbing the laser light, and is, therefore, copper, as this is

a recognised phenomenon (the artefact at around 400 cm^{-1}, labelled at 395 cm^{-1} in the processed spectrum, appears in the spectrum when the received intensity is low).

However, aside from the low intensity, the processed spectrum reveals some peaks - at 554, 760, 1090 and 1628 cm^{-1}. The 554 and 1090 cm^{-1} peaks could be attributed to lapis lazuli, which would mean that the green is vergaut - a mixture of a blue and a yellow colourant, in which lapis lazuli is the blue.[11] Alternatively, the lapis lazuli peaks could be a result of contamination, given the close proximity of the green to the blue. The 760 cm^{-1} and 1628 cm^{-1} peaks do not have an obvious identification - no yellow mineral colourant yields peaks at that wavenumber, and the peaks do not correspond with any other mineral pigment, green or otherwise.

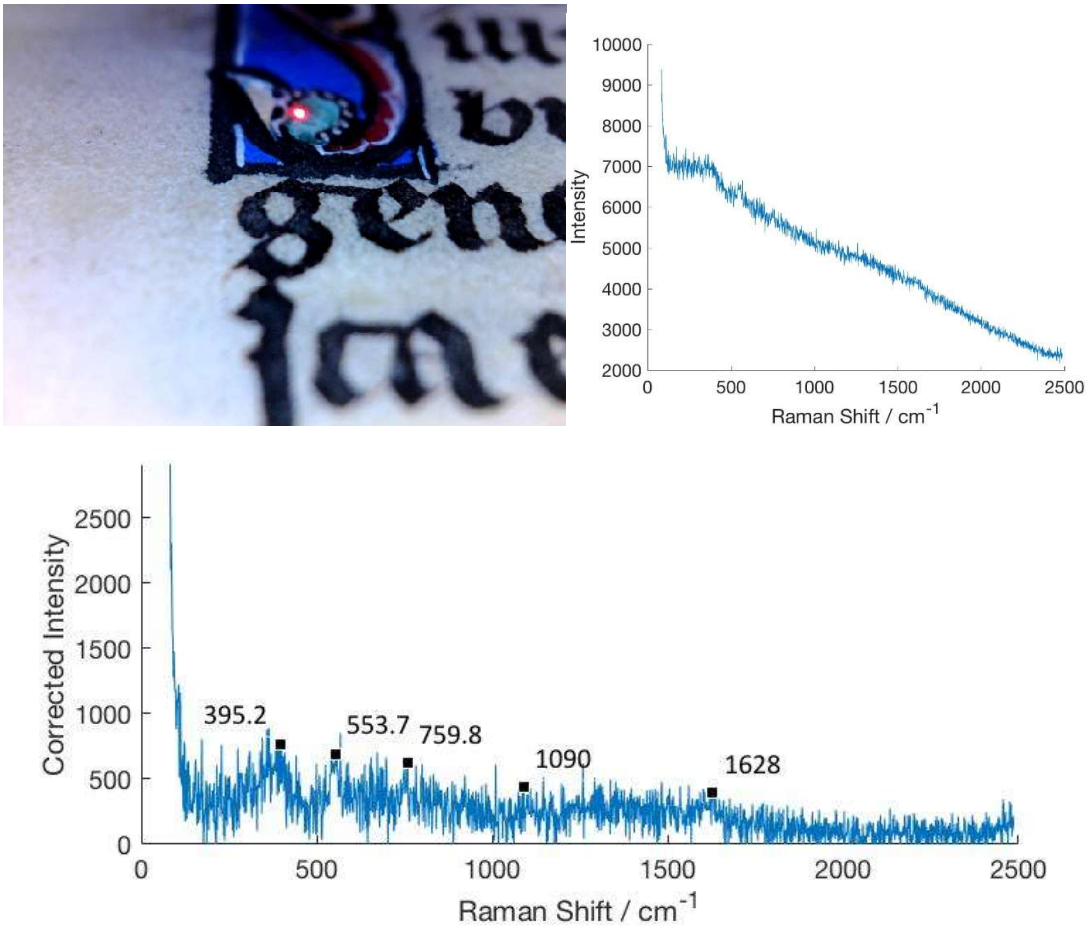


Figure 18: (top left) The spot on fol. 401 r that was examined by Raman spectroscopy, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

[11] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1491.

The green clothing on fol. 3v was examined with FORS, and the spectrum obtained is shown below in Figure 19. The spectrum gives an absorbance maximum of 718 nm - consistent with that given in published data for verdigris, a copper-based pigment.[12]

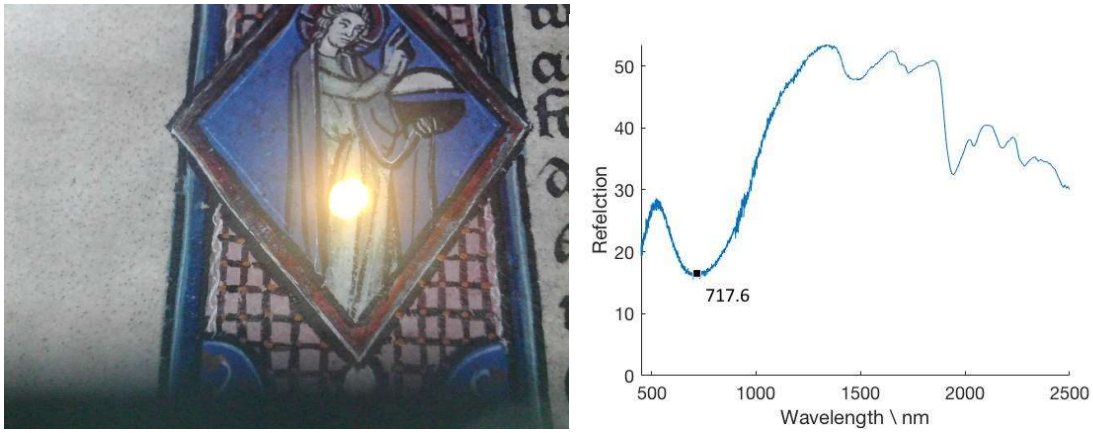


Figure 19: (left) The green examined by FORS in fol. 3 v, and (right) the spectrum obtained.

Use of black

Like the other manuscripts in this study, black is used to outline depictions and decorations, and to colour such areas and objects as necessitated by the nature of the scene. The black outline on fol. 1 r was sufficiently wide enough to be examined with Raman spectroscopy, and the spectra obtained are shown in Figure 20 below. It is possible to see the broad 1584 cm^{-1} peak in the raw spectrum, and in the processed spectra. This consistent with the range of peaks given for carbon in published data (at 1324 cm^{-1} and a broad peak 1594 cm^{-1}).

[12] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

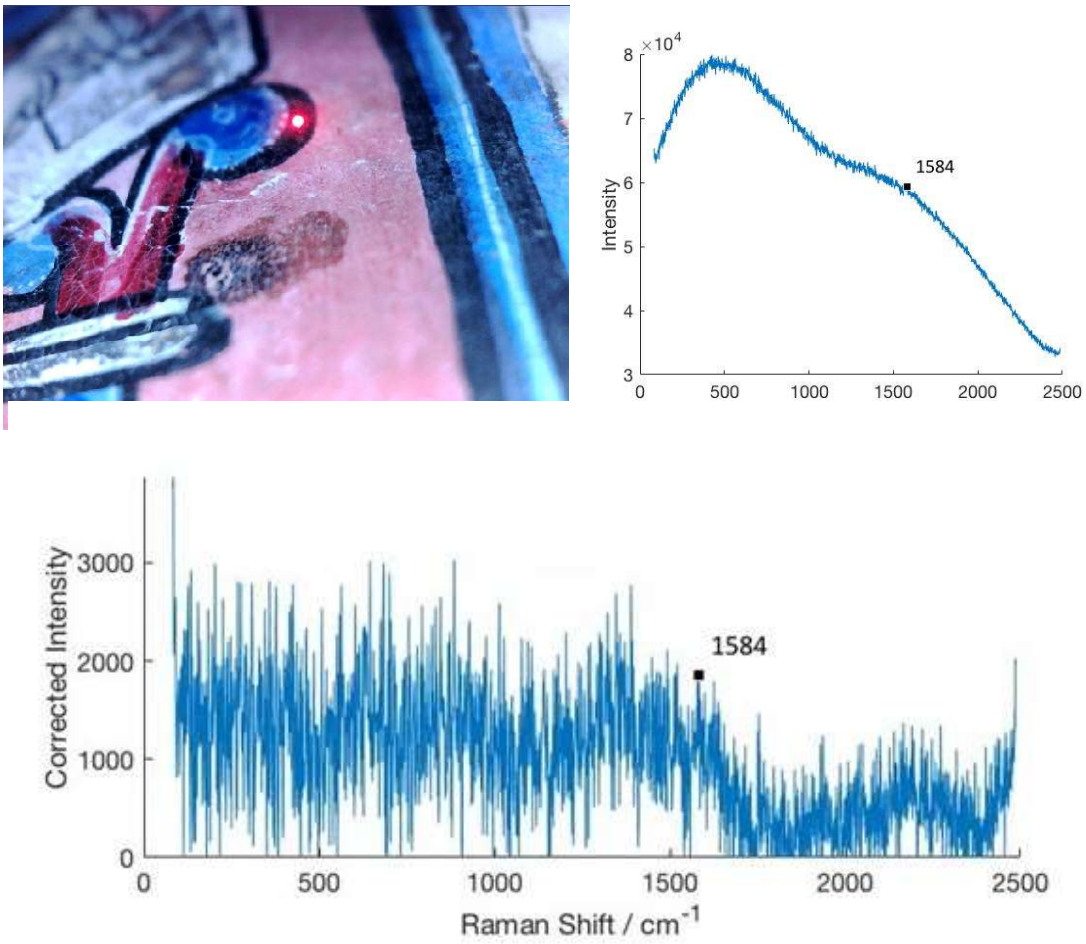


Figure 20: (top left) The spot on fol. 1 r that was examined by Raman spectroscopy, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

The black on fol. 1r was also examined with FORS and found to be carbon, due to the featureless spectrum, particularly in the visible region of the spectrum, and the low reflectance. The apparent feature from 450 to 490 nm is an aberration and should be ignored.

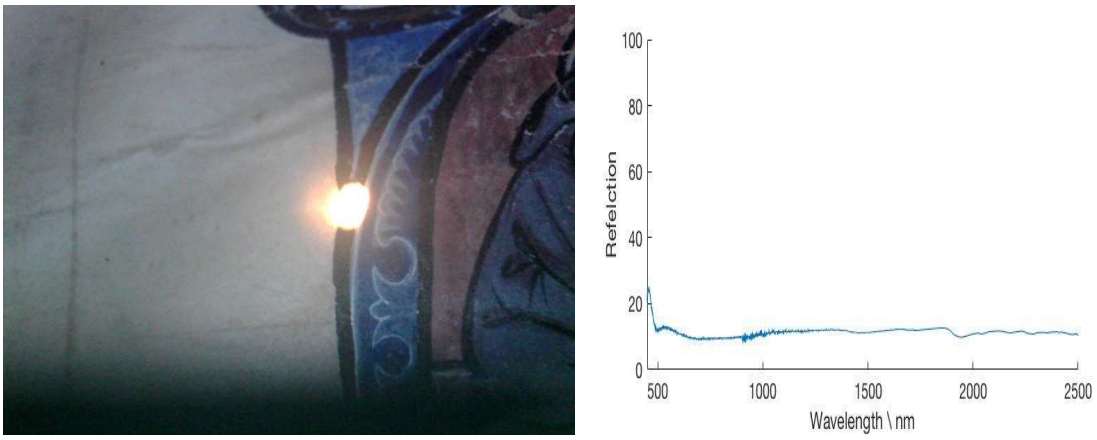


Figure 21: (left) The black outline on fol. 1r examined by FORS, and (right) the FORS spectrum obtained.

Use of pink

Alongside blue, pink is the most used pigment in NCO MS 1, seen in the ground of initials as well as in the decoration of the initial itself. The pink ground on fol. 1 r was examined with both Raman and FORS, and the results are shown in Figure 22 and Figure 23, respectively. The Raman spectrum yielded nothing but fluorescence. However, the FORS spectrum reveals an absorbance maximum of 559 nm, which is almost exactly that given in published data for brazilwood (at 600 nm). Brazilwood is further described in Chapter Two. Although orcein has an absorbance maximum at 595 nm, its use is discounted as its FORS profile displays a double absorbance maximum, not seen here.

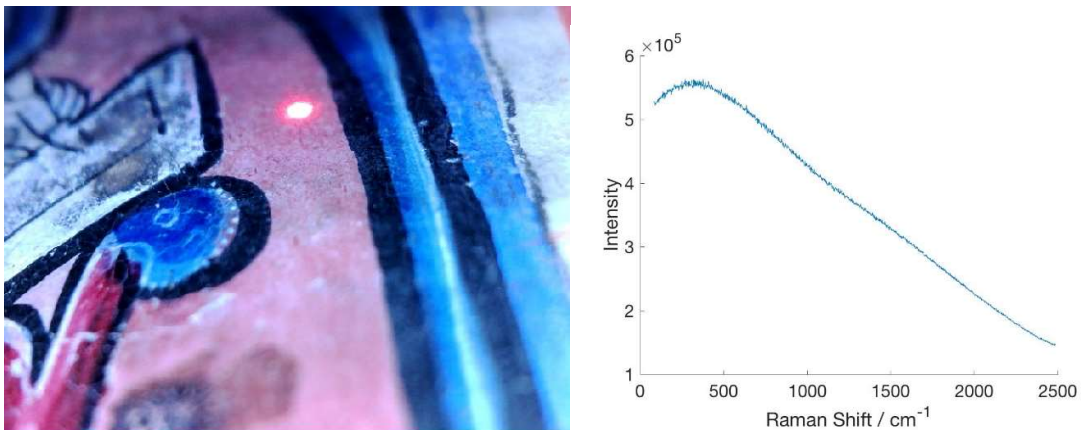


Figure 22: (left) The spot on fol. 1r examined, and (right) the raw spectrum obtained.

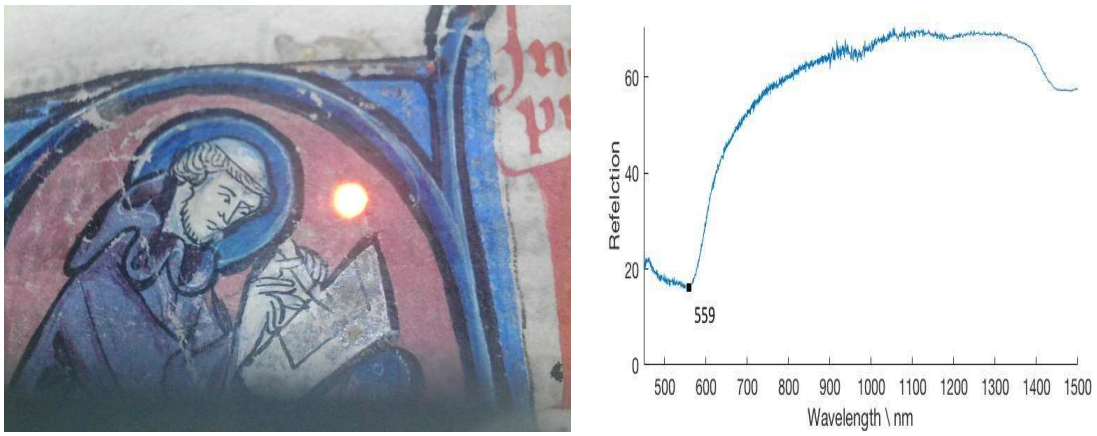


Figure 23: (left) The spot on fol. 1r examined, and (right) the spectrum obtained.

Use of purple

As mentioned in the overview above, two purples are used in NCO MS 1, one that is used to contour clothing and one that is used to colour objects, the column head on fol. 1 seen in Figure 1, for example. It may be that these are in fact the same colourstuff deployed in different ways and thus seeming to be different colours but, as this is not certain, the colours were examined separately.

Figure 24, shows the spectra obtained when the purple colouring the column head was examined. Although there is a very broad peak in the raw and processed spectrum, centring on 1387 cm^{-1}, it is likely to be fluorescence, indicating that the purple is from an organic source. In this instance, background subtraction is not helpful as it is creating an artefact in the subtracted spectrum.

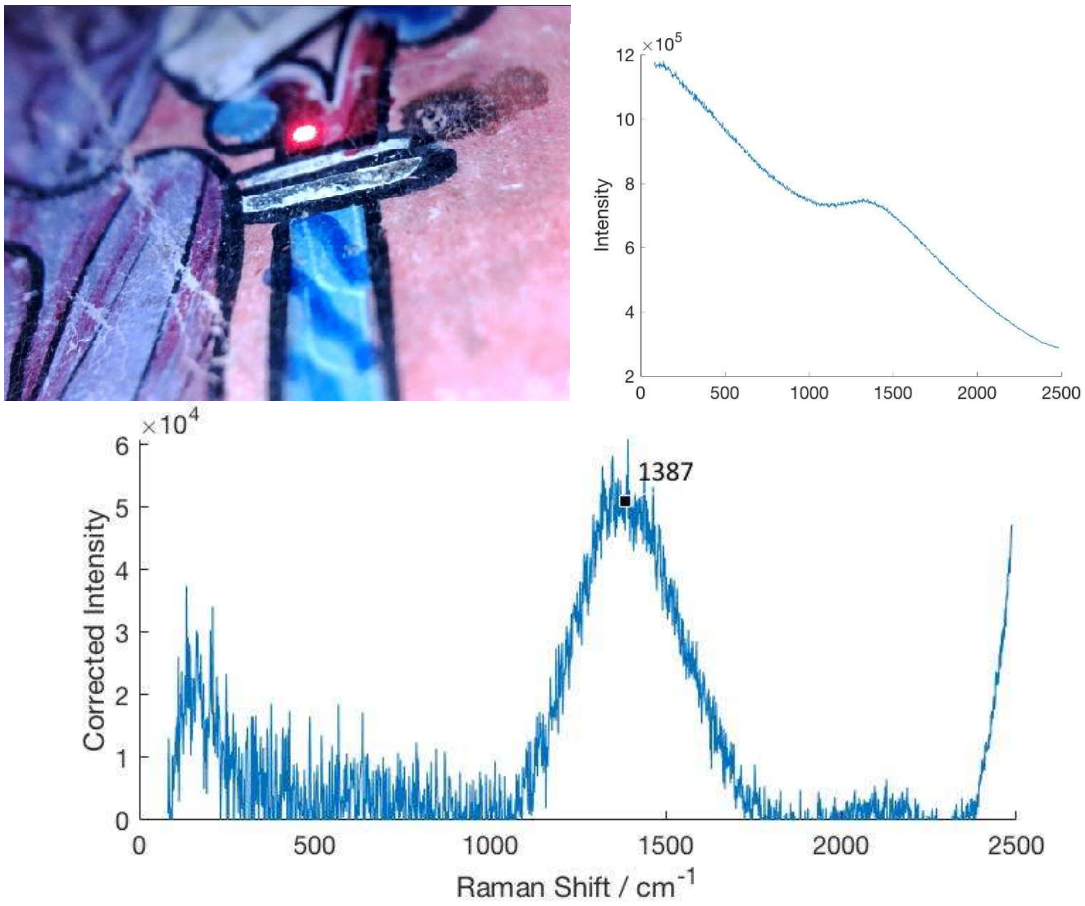


Figure 24: (top left) The spot on fol. 1r that was examined by Raman spectroscopy, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

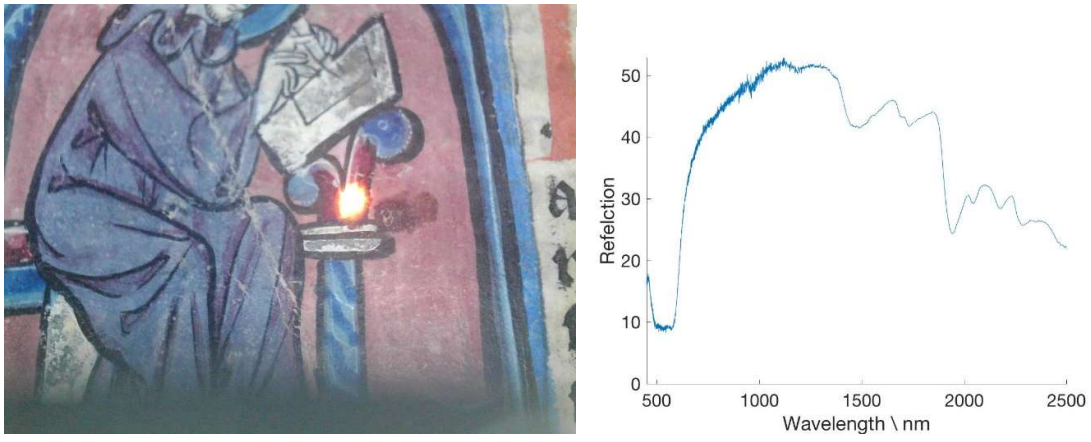


Figure 25: (top left) The spot on fol. 1r that was examined by Raman spectroscopy, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

Interestingly, when the same purple area was examined by FORS, the resulting spectrum appeared to have two absorbance maxima. In order to ascertain these absorbance maxima more easily, the Kubelka-Munk formula was applied, with the resulting spectrum shown below in Figure 26.[13] This transformation allows the two absorbance maxima to be seen more clearly - at 540 and 574 nm. Double absorbance maxima are associated with organic red and purple dyes.[14]

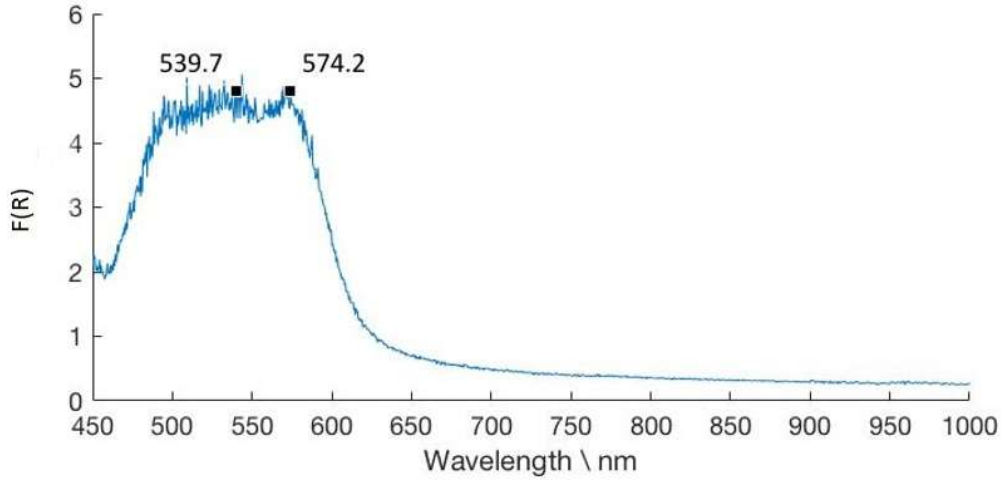


Figure 26: A plot of the FORS spectrum of the purple on fol. 1r after Kubelka-Munk transformation.

[13] The Kubelka-Munk theory is discussed further in Chapter 4.

[14] Maurizio Aceto et al., 'A Diagnostic Study on Folium and Orchil Dyes with Non-Invasive and Micro-Destructive Methods', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 142 (May 2015): 159–68.

When compared to the spectral features of known samples of purple dyes, as seen in Figure 27, the spectrum of the purple in question (re-plotted again with wavelength against log (1/R) for ease of comparison) looks similar to that for Tyrian purple and folium.[15] The purple examined in NCO MS 1 has absorbance maxima of 540 and 574 nm, whilst that in published data for folium is given as 545 and 580 nm. Tyrian purple is reported as having has only one maximum, at 530 nm, and is described as having 'a shoulder'. Given that Tyrian purple is unknown in manuscripts of this date and place, and that no Raman spectrum of Tyrian purple was seen, and given further that the FORS spectrum seems to have two absorbance maxima, not one, its presence here can be discounted. By contrast, the use of folium is a strong possibility, as the published absorbance maxima of 545 nm and 580 nm are not too dissimilar from those obtained from the purple in question - at 540 and 574 nm.

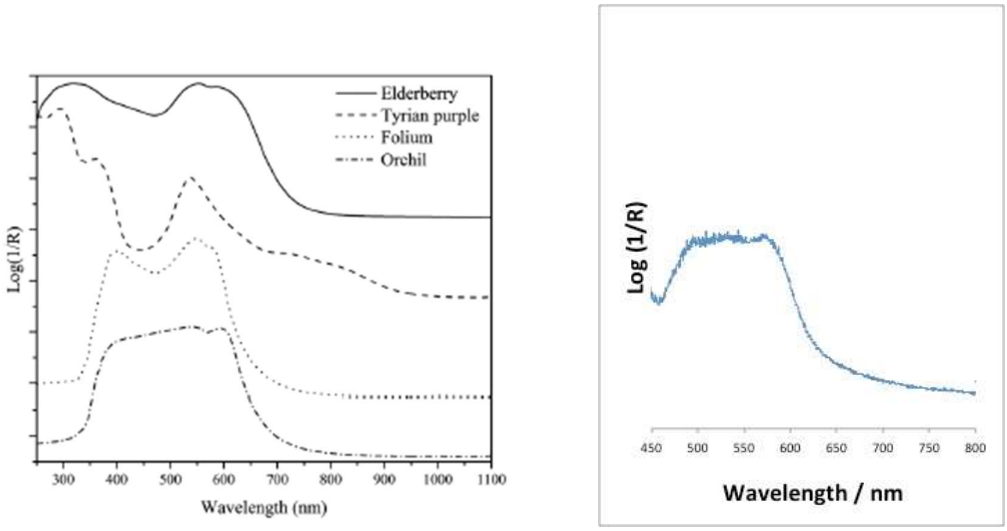


Figure 27: (left) A chart showing the different spectral features of purple dyes (Aceto et al.), and (right) the Log (1/R) plot of the purple on fol. 1r.

[15] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

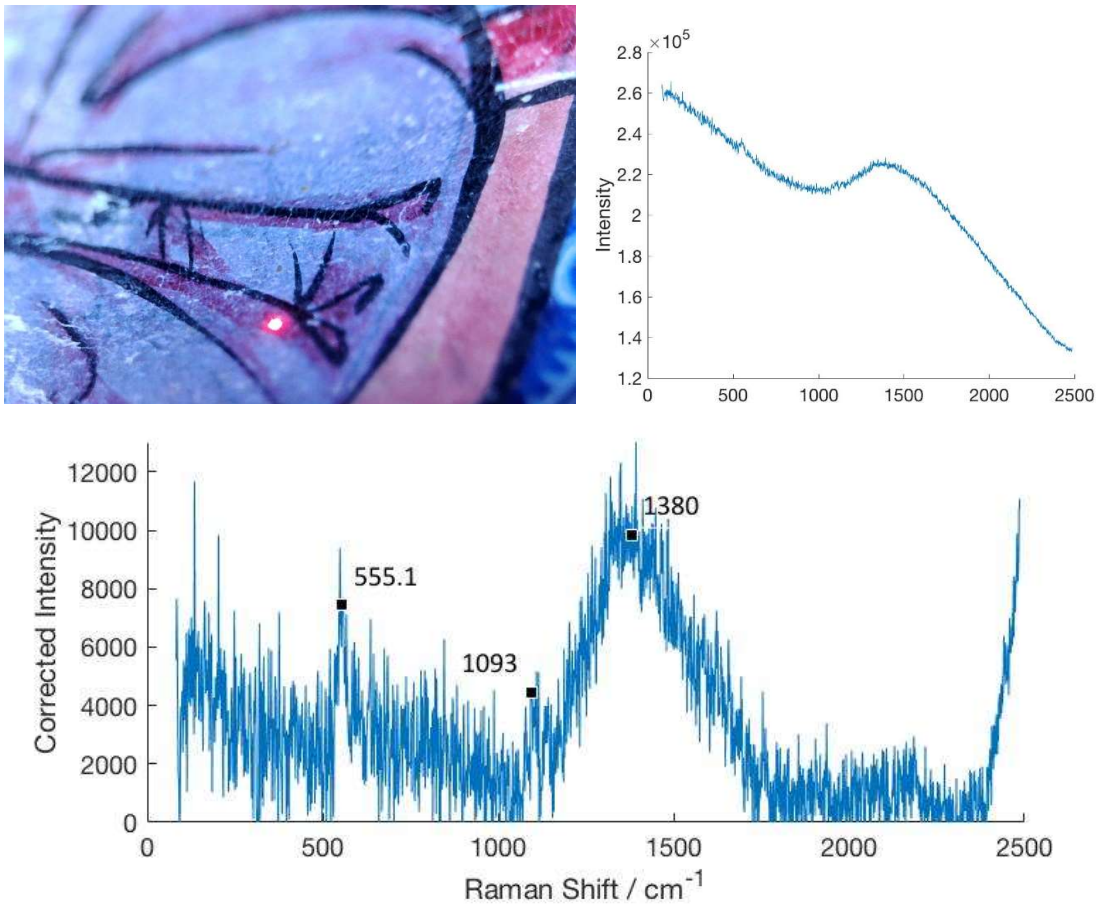


Figure 28: (top left) The spot on fol. 1 r that was examined by Raman spectroscopy, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

The purple overlay on the blue-grey gown on fol. 1r was examined with Raman spectroscopy and, interestingly, records the same pattern of fluorescence (centring on about 1380 cm^{-1} in the processed spectrum) as seen in the pure purple on the same page. Whilst not diagnostic, this suggests that the two purples could be the same. Aside from fluorescence, the Raman spectrum records peaks of 555 and 1093 cm^{-1} which can be seen in the raw and processed spectrum and can be attributed to the underlying lapis lazuli of the blue-grey cloak on which the purple sits.

Use of white

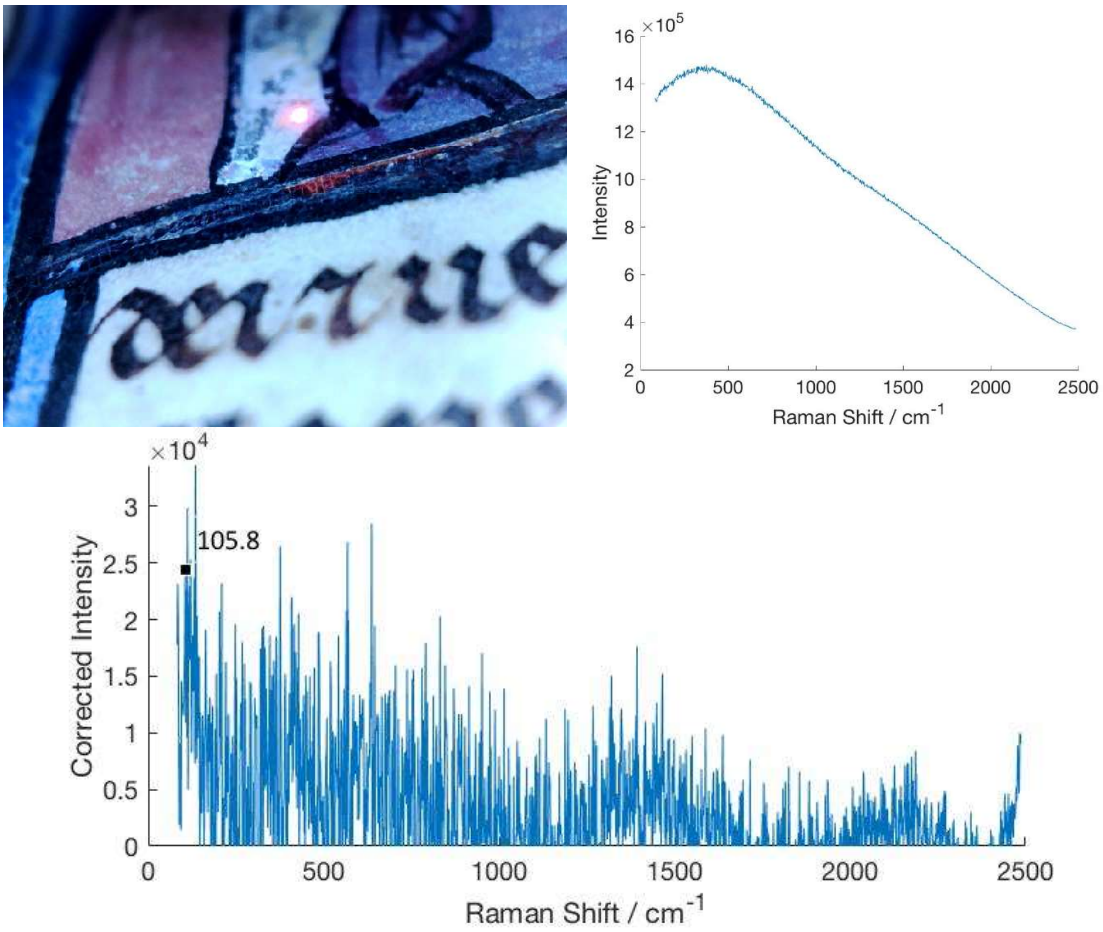


Figure 29: (top left) The spot on fol. 1 r that was examined by Raman spectroscopy, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

Figure 29 shows an area of white lead examined by Raman spectroscopy, with the resultant spectra showing one peak attributed to white lead, at 106 cm^{-1} (in published data this is quoted at 104 cm^{-1}). [16] Another white area, on fol. 401r, was examined by FORS and also found to be white lead, due to the absorption band at 1448 nm (which is quoted at 1447 nm, in published data). As seen in other manuscripts white lead is a common pigment, often employed for flesh and for colouring white objects, and in lines and dots on top of other colours that add to the decoration and seem to extend the palette.

[16] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

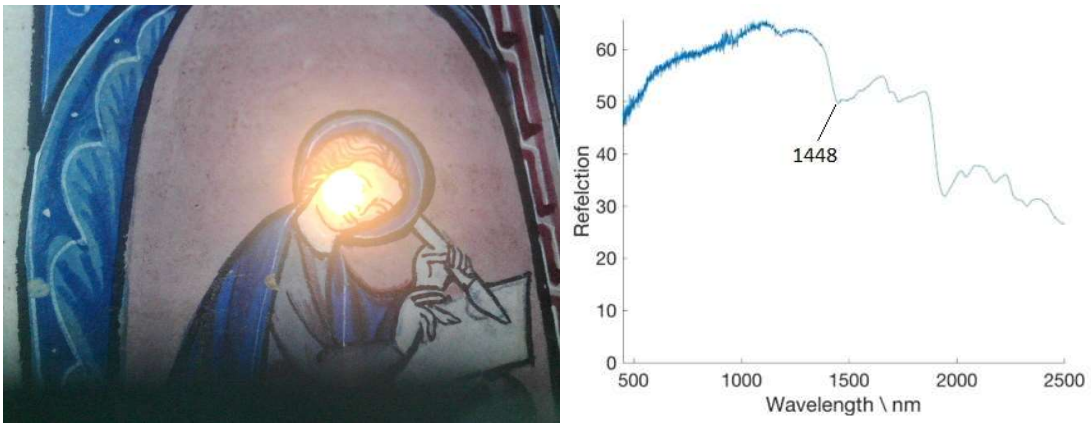


Figure 30: (left) The spot on fol. 401 r that was examined by FORS, and (right) the labelled raw spectrum obtained.

Use of gold

Unusually for a thirteenth-century manuscript of this grade, NCO MS 1 contains no gold, as demonstrated by the full-page images of fol. 1r and fol. 3v in Figure 12 and Figure 17 above, and the close-up image in Figure 31 below from fol. 401r.The proficiency with which the decoration was carried out would suggest that its makers were not unskilled, so the inability to apply gold is an unlikely reason for its absence. Similarly, Paris in the thirteenth century was certainly not short of gold, so again, supply cannot be the reason. Nor, given that the illuminators made lavish use of expensive lapis lazuli, is economic restraint likely to have been involved. Consequently, it may be assumed that this reflects the preference of the artist or the taste of the patron.

Figure 31: A close up of the initial on fol. 401r.

Text and text ornamentation

Text

The black text on fol. 1 r was examined by Raman spectroscopy and FORS. Figure 32 shows that no peaks were seen in the Raman spectrum, meaning that carbon is unlikely to be present.

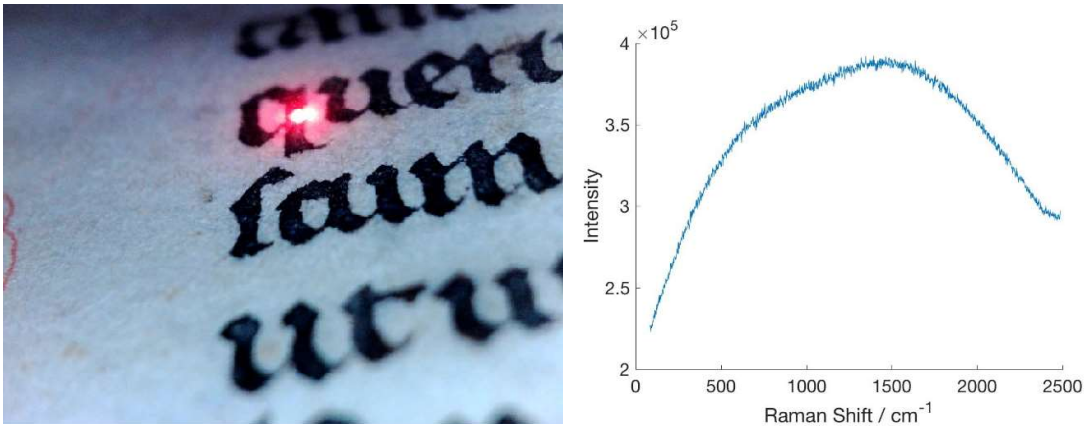


Figure 32: (left) The spot on fol. 1r where the ink was examined by Raman spectroscopy, and (right) the spectrum obtained.

The FORS spectrum, seen below in Figure 33, indicative of iron gall ink without any carbon, confirms this.

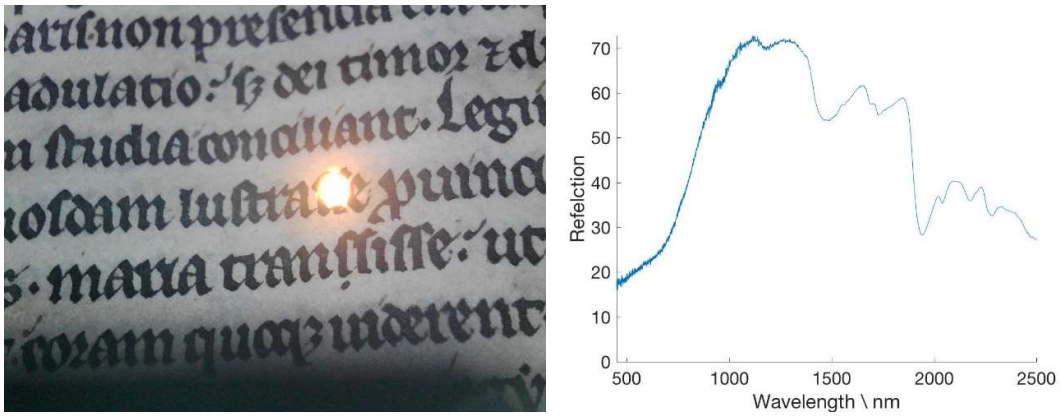


Figure 33: (left) The spot on fol. 1 r where the ink was examined by FORS, and (right) the spectrum obtained.

Display script

As seen below in Figure 34, Figure 35, Figure 36 and Figure 37, the red and blue display scripts on fol. 1r (seen in full in Figure 12) were examined by both Raman spectroscopy and FORS.

The red script is vermilion, evidenced by the peaks in the Raman spectrum at 258 and 350 cm^{-1}, which correspond to those in published data at 251 and 342 cm^{-1}. This is confirmed by the FORS spectrum, which has an inflection point of 602 nm, almost exactly the same as that in published data at 600 nm. [17]

[17] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222; Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

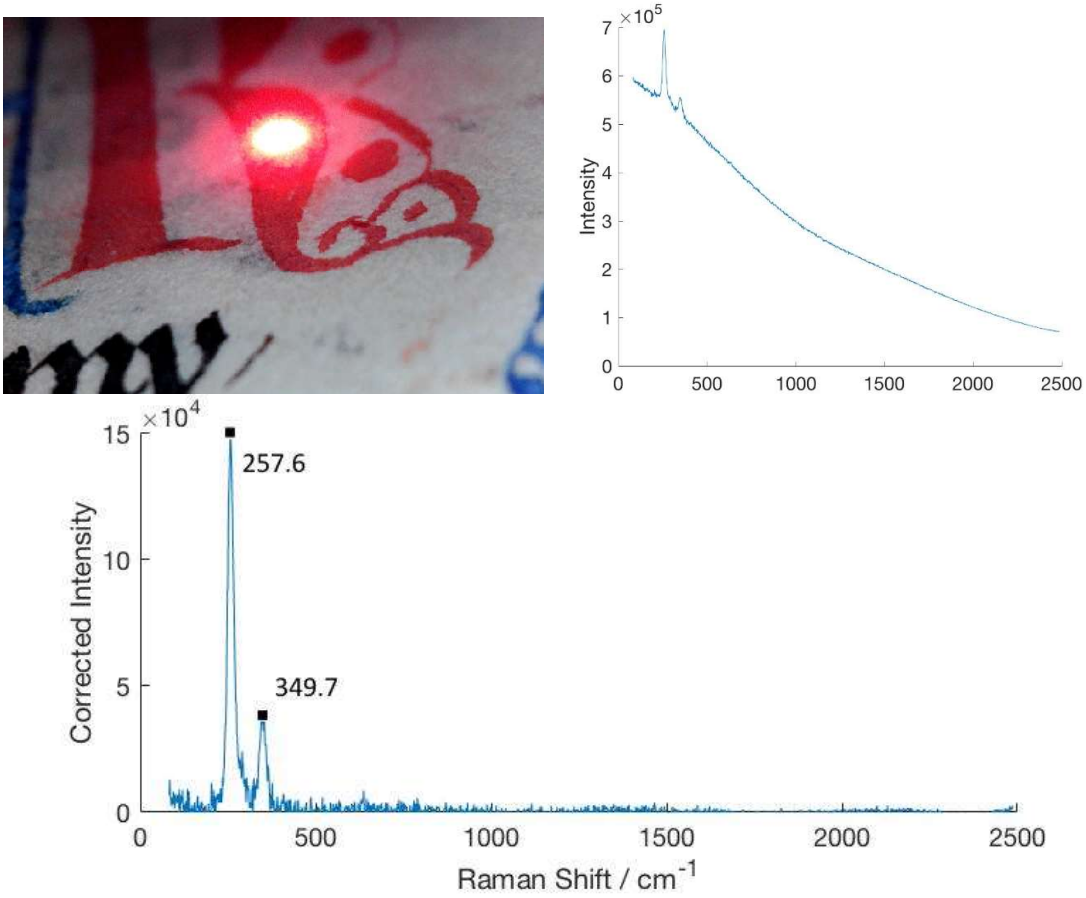


Figure 34: (top left) The red display script examined by Raman on NCO MS 1 fol. 1 r, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

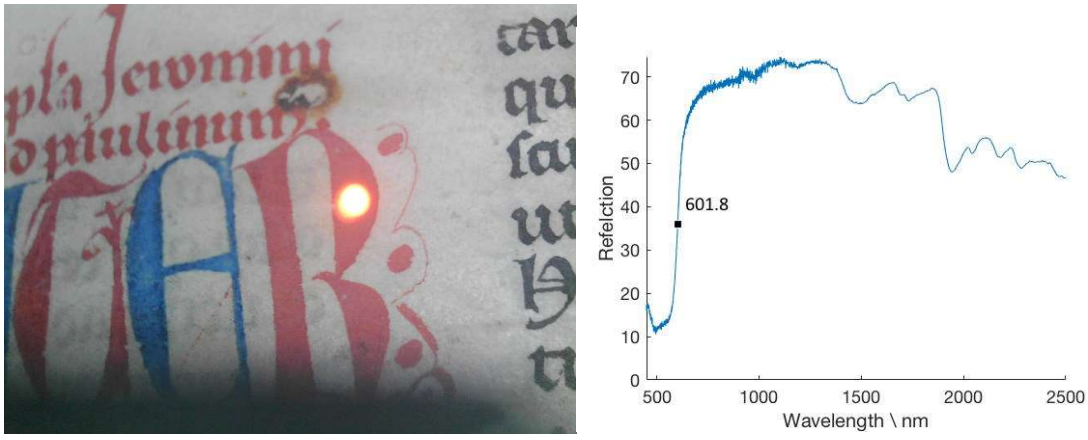


Figure 35: (left) The spot on fol. 1 r examined by FORS and (right) the spectrum obtained.

The blue script does not return a Raman spectrum with any peaks and, as evidenced by the low intensity of the spectrum, is absorbing the laser light - a common feature when copper-based

pigments are examined. The FORS spectrum reveals the pigment to be azurite - defined by the peaks at 2285 and 2354 cm^{-1} which are similar to those in published data at 2285 and 2352 cm^{-1}, and also by the absorbance maximum at 649 nm, close to that in published data at 640 nm. [18]

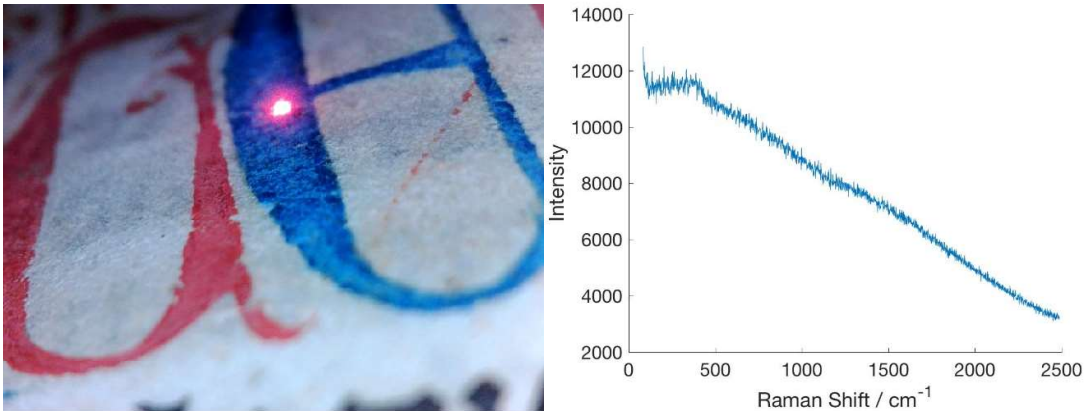


Figure 36: (top left) The blue display script examined by Raman on NCO MS 1 fol. 1 r, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

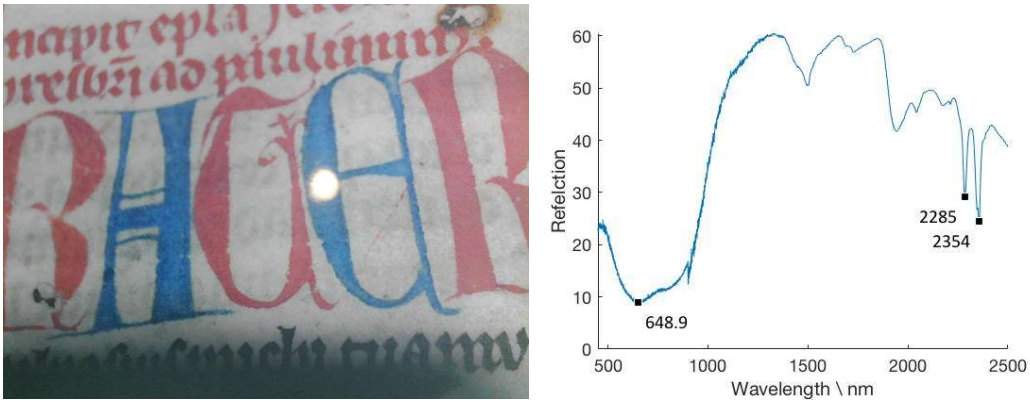


Figure 37: (left) The spot on the blue display script on fol. 1 r examined by FORS and (right) the spectrum obtained.

Rubric

Figure 38 shows the spot on fol. 401r, where the red rubric was examined with Raman spectroscopy, and the corresponding spectra obtained. The peaks at 256 and 347 cm^{-1} are consistent with those for vermilion.

[18] Mulholland et al., 'Identifying Eighteenth Century Pigments at the Bodleian Library Using in Situ Raman Spectroscopy, XRF and Hyperspectral Imaging', p. 11; Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p.1491.

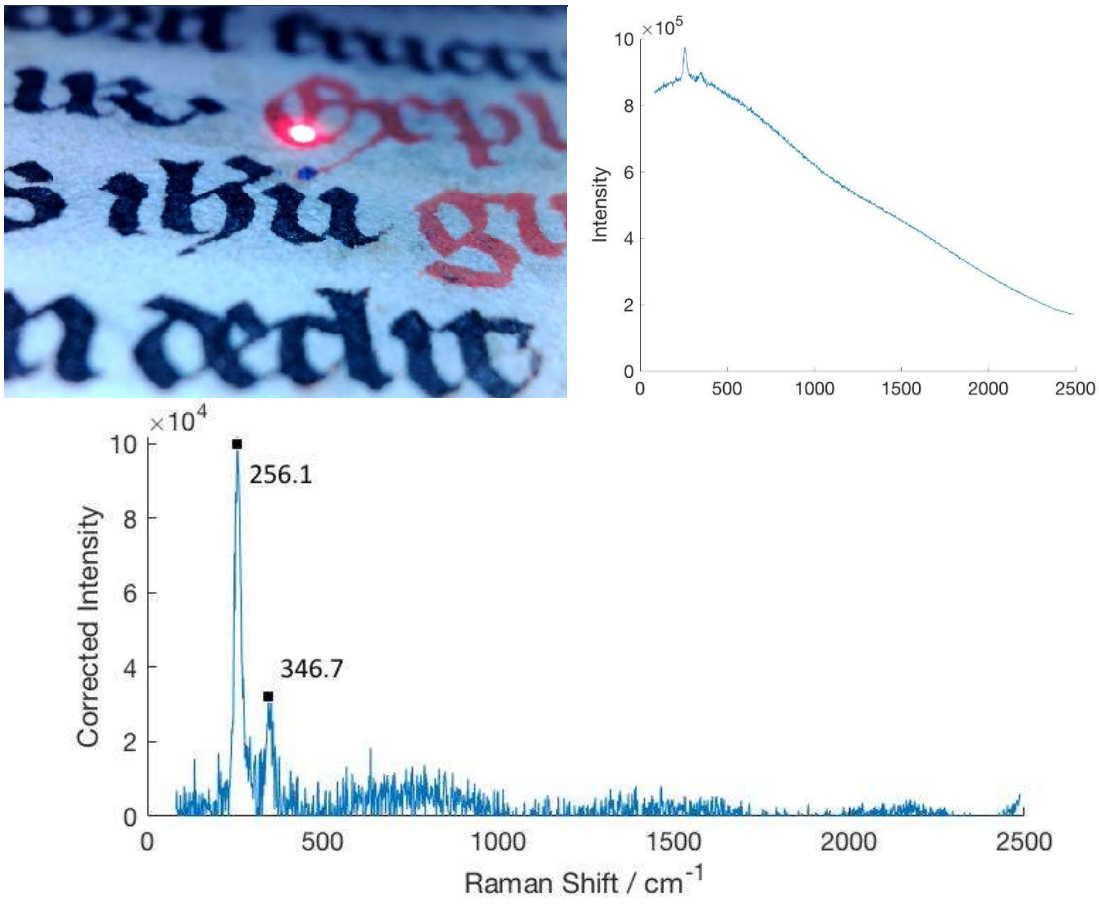


Figure 38: (left) The spot on the rubric on fol. 401 r examined with Raman Spectroscopy, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

Text initial and flourishing

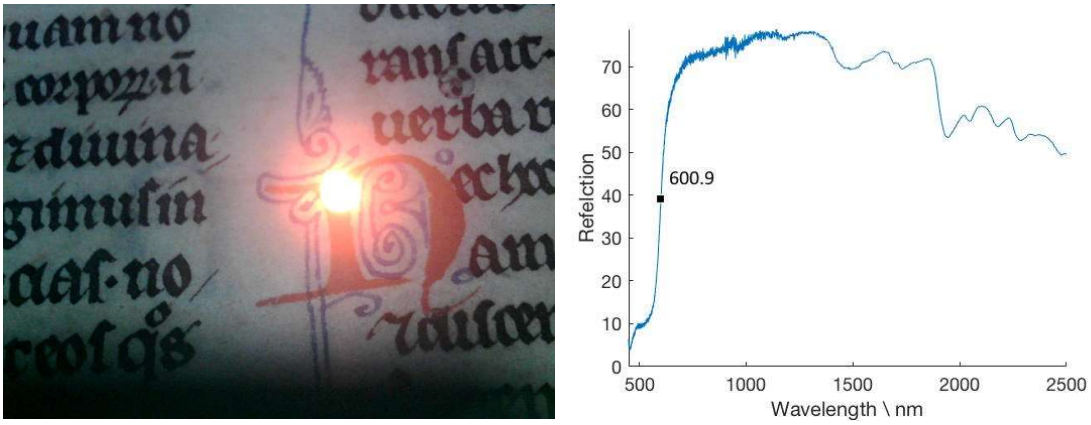


Figure 39: (left) The spot on the red initial examined by FORS on Fol. 1 r, and (right) the resulting spectrum.

A red text initial flourished with blue on fol. 1 r was examined with FORS, and the results are shown below. The red gives a FORS spectrum with an inflection point of 601 nm, shown in Figure 39, which suggests vermillion (in published data, the inflection point is given as 600 nm).

Figure 40 shows the FORS spectrum obtained from the blue flourishing. As can be seen, there is no clear absorbance maximum, and no clear inflection point, rendering identification of the pigment difficult. The pigment is unlikely to be azurite, as its absorption bands are usually clearly seen. In principle, therefore, it could be either lapis lazuli or indigo; however, as the former was rarely employed for flourishing, while the latter was regularly used thus, the colourant is likely to be indigo. A definitive identification via Raman spectroscopy could not be taken.

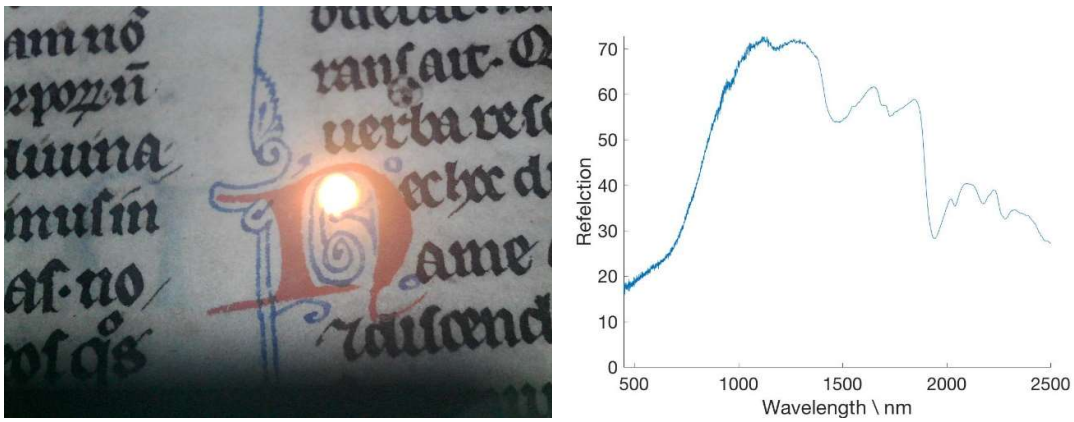


Figure 40: (left) The blue flourishing examined by FORS on fol. 1 r, and (right) the spectrum obtained.

Red edging

One feature of the book that is not medieval, but interesting nevertheless, is that the book has at some point in its later history been re-bound and its edges painted red. This red paint has seeped into some of the pages of the manuscript, and when examined by Raman spectroscopy, was found to be vermilion with peaks at 261 and 345 cm^{-1}.The FORS spectrum returned a spectrum with an inflection point of 595 nm, consistent with the 600 nm for vermilion in published literature.[19]

[19] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222; Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

The choice of vermilion here may have been motivated by more than aesthetic considerations for, being highly toxic, it may have been added to deter insects such as woodworm and rodents from damaging the book.[20]

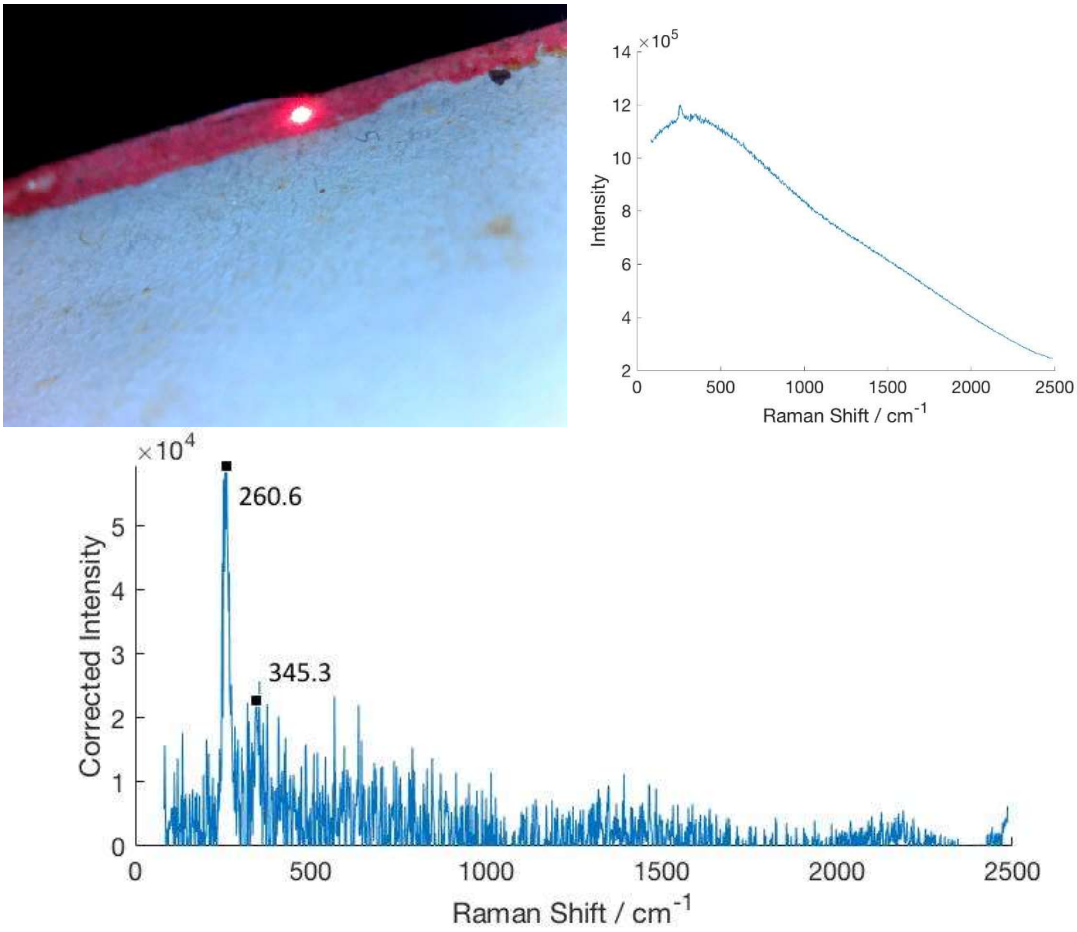


Figure 41: (top left) The spot on fol. 1 r that was examined by Raman spectroscopy, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

[20] However, as it is toxic to pests, it is also toxic to humans - no one at New College Oxford seemed to be aware, during our visit, that they were handling toxic material!

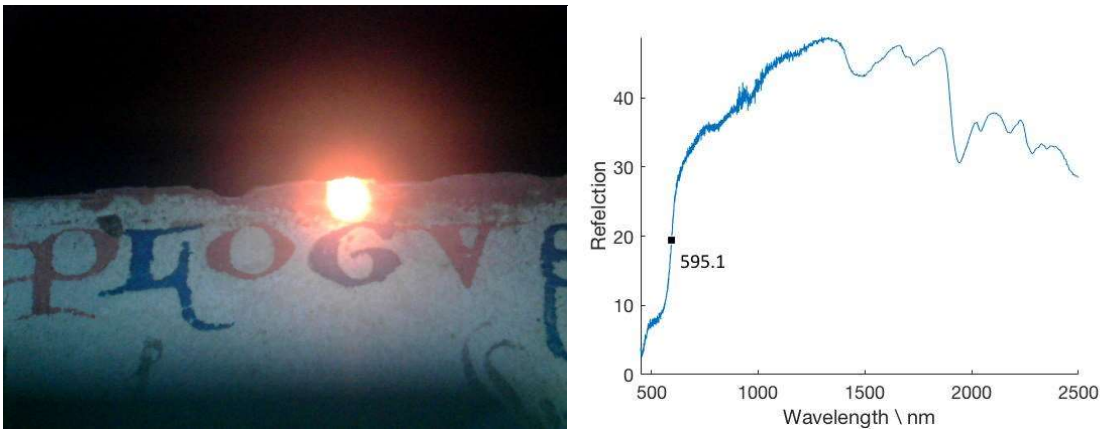


Figure 42: (left) The area of the red paint on fol. 1 r examined by FORS, and (right) the spectrum obtained.

Further comments on the palette as a whole

This high-grade manuscript is typical for its time and date, in that it is awash with lapis lazuli, and uses an, as yet, unidentifiable organic pink to contrast with the blue. The other pigments employed are also common in the thirteenth century and include red lead used for orange, a copper green, white lead, lapis ash, vermilion and carbon. Azurite is also employed, and its manner of application - for tonal contrast with lapis lazuli in the same area of the illumination- indicates that azurite was employed for artistic effect rather than as an economic necessity. Potentially indigo is used for flourishing, and the ink seems to be oak-gall ink.

Unusually for the manuscripts seen in the study, the manuscript employs two purples. One is probably folium, and one cannot yet be identified. However, this unidentified purple may also be folium applied in a different way. Furthermore, the fact that the manuscript does not use gold is unusual.

New College Oxford MS 20

Notes

New College Manuscripts NCO MS 1 and MS 20 were examined *in situ* at New College Library, Oxford, in late February 2020. We must impose upon our hosts by requiring the use of a room with suitable space that can be made dark, and it is usual to have a member of staff from the host institution present. Naturally, these factors limit the time we have to examine manuscripts, and so the data collected here is that which could be collected during the few hours available.

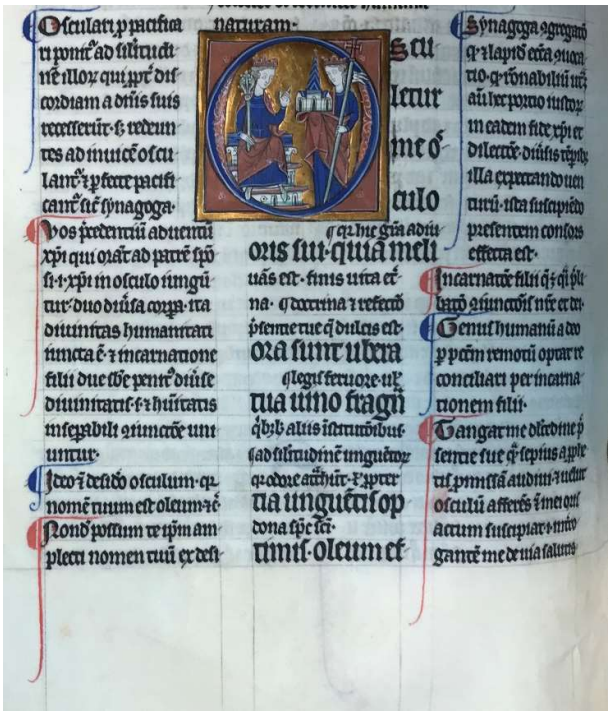


Figure 43: NCO MS 20, Cantica (fol. unknown).

Description and provenance

NCO MS 20 is a part-bible with gloss, which was an alternative form in which biblical texts were circulated during the thirteenth century. As such, it not a pocket-sized book made for prayer but a larger one made for study and reflection. It dates from the middle of the thirteenth century and was

likely made in Southern England. Nothing is known of its history until it reached New College as a gift by the founder William of Wykeham (1324-1404), once Bishop of Winchester.[21]

Codicology

Text layout, ornamentation, and rubrics

As can be seen in Figure 44 below, the text is laid out in various formats typical for a glossed book of its date. The text is generally set out in three columns with the biblical verses at the centre in larger script, written on every other line and the gloss to either side of them, occupying every line. Further interlinear glosses are added between the lines of the biblical text.

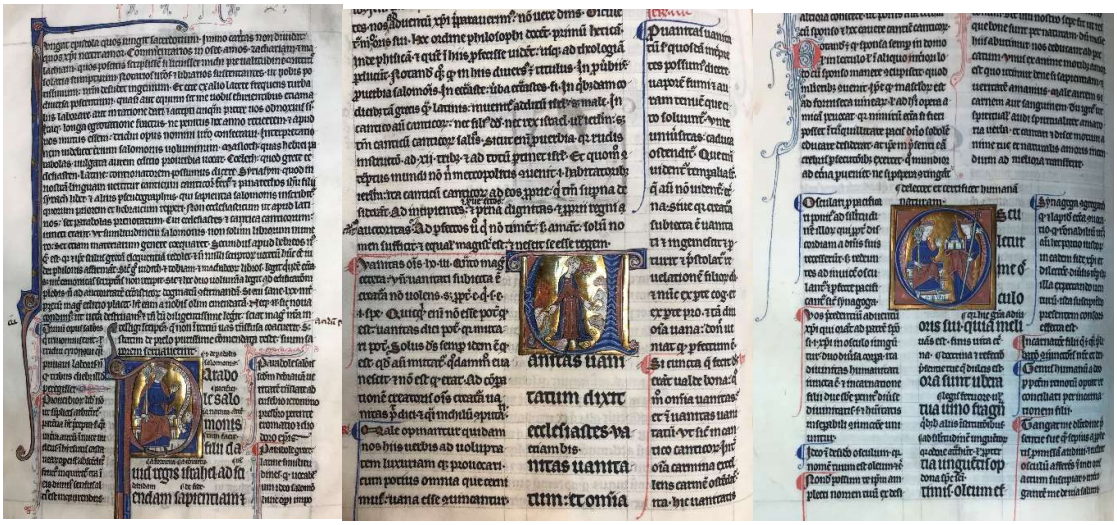


Figure 44: (left to right) NCO MS 20 Fols. 1r, 63v and Cantica (folio unknown) showing the use of different column sizes.

Script

The script is Textualis quadrata, evidenced by the fact that the minims invariably terminate in a diamond shape despite the size of the text, seen clearly in Figure 45 below. This script is indicative of a high-grade manuscript.

[21] Coxe, *Catalogus codicum mss. qui in collegiis aulisque oxoniensibus hodie adservantur*; Bodleian Library, 'MLGB3 Home'.

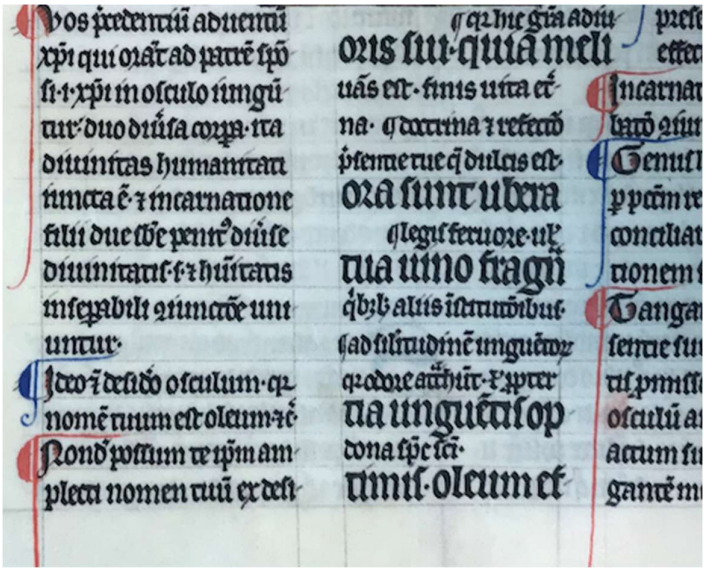


Figure 45: Text from NCO MS 20 Cantica (fol. unknown).

Artwork

Style of artwork

The style of the artwork is similar to those seen in previous manuscripts in this study, with historiated initials conveying a scene relevant to the text, surrounded by decorated initials - all deployed with a limited palette with blue and a contrasting colour (in this case a dark red-brown) the principal colours.

Approach to painting

Figure 46: Close-up of the initial on fol. 63v.

The artwork in NCO MS 20 is of a high standard, and much use is made of the limited palette to produce visually stunning effects. The upright of the initial on fol. 63v seen above in Figure 46, for example, gives an optical illusion effect of movement and depth. When coupled with the shine and three-dimensional burnish of the gold, and the detailed painting of colours and folds seen in the drapery, the drawings make a feast for the eye. The richness of the colours and the attention to detail - in the drawings of the animals for example - adds to the impression that this was a manuscript that had time, care, and money lavished upon it.

Palette

Overview

The initial shown in Figure 46 exemplifies the palette of colours in New College NCO MS 20. Gold is employed in quantity, burnished to a high sheen and, in the initial above, tooled for effect. A vivid blue is deployed for drapery with the same rich blue, in varying shades, used for infills. Similarly, a brown-red colour in different shades is utilised both in the drawings and as infill in the initial.

White is employed for hands, faces and other objects; in the case above it is also employed for several of the animal heads that appear. Like other manuscripts examined so far, a vibrant orange and a vibrant green are employed sparingly to denote particular small items or to highlight delicate

features. In Figure 46, orange is utilised for just one animal, and to colour one fold in the clothing, whilst green is also applied to colour just one animal. Black is used as an outline, and to colour small items in the scenes, such as shoes. Two tiny areas of yellow, so small that they could easily be missed, were seen on one folio of the manuscript, as an over-painting in the decoration of an initial.

Clever use of different shades of colour, combined with detailed white overpainting, mean that some stunning visual effects are created - the upright of the initial 'U' in Figure 46, for example, contains only a light and dark blue with white lines painted over, and a black outline - but the effect is an eye-catching pattern with the impression of a much larger palette.

Use of Blue

A vibrant blue is used for clothing, with darker shades to indicate folds of the cloth. The same rich blue is deployed for infills, with darker and lighter shades to give the colour depth. Both the clothing and the infill background can be seen above in Figure 46.

As evidenced in Figure 47, the blue is a mixture of lapis lazuli and azurite. The spectrum shows an absorbance maximum of 604 nm, consistent with that for lapis lazuli in published data, whilst the two absorbance bands at 2285 and 2358 nm are consistent with those given for azurite in published work, where they are reported as being at 2285 and 2352 nm.[22] The absorbance maximum of azurite is 640 nm, and one might expect to see a shift in the maximum detected, from 600 nm towards 640 nm, with an increasing percentage of azurite. The fact that the maximum remains close to 600 nm, along with the fact that the absorbance bands are small (when compared to that of the azurite seen in Figure 72 for example) suggest that there is only a small percentage of azurite in the lapis lazuli. Further details about the mixing of pigments and the resulting changes to FORS spectral features are given in Chapter Three.

[22] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491; Mulholland et al., 'Identifying Eighteenth Century Pigments at the Bodleian Library Using in Situ Raman Spectroscopy, XRF and Hyperspectral Imaging', p. 11.

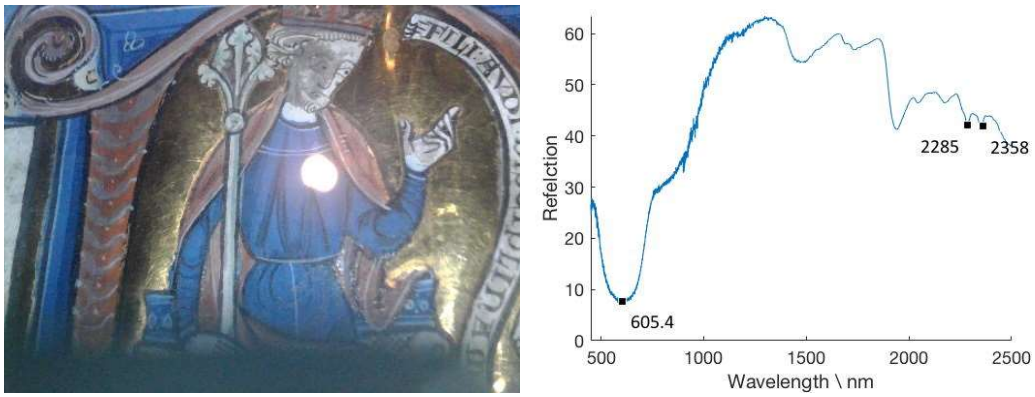


Figure 47: (left) The spot on NCO MS 20 fol. 1 r where the blue pigment was examined, and (right) the FORS spectrum obtained.

Mixing lapis lazuli and azurite is not uncommon, and as previously discussed, may be a result of artistic preference, economy or supply.[23] In a manuscript that is replete with gold and blue such as this one, it would seem likely that economy and supply of lapis lazuli are not considerations, and that the choice is, therefore, an artistic one, with the colours being mixed in order to create the vibrancy and range of blues seen.

To confirm the use of lapis lazuli, a Raman spectrum of the lighter blue and the darker blue was taken, as seen in Figure 48 and Figure 49 below. In Figure 48, the lighter blue, the peaks at 274, 551 and 1101 cm^{-1} correspond to those given in published works and in Figure 49 the darker blue; the peaks at 265, 554 and 1103 cm^{-1} similarly correspond.[24] Interestingly, both raw spectra show fluorescence (which accounts for the artificial feature in the processed spectra at around 1300 cm^{-1}). This is likely due to the organic nature of the binder used.

[23] Gameson et al., 'Late Medieval English Illuminators' Blues'.

[24] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

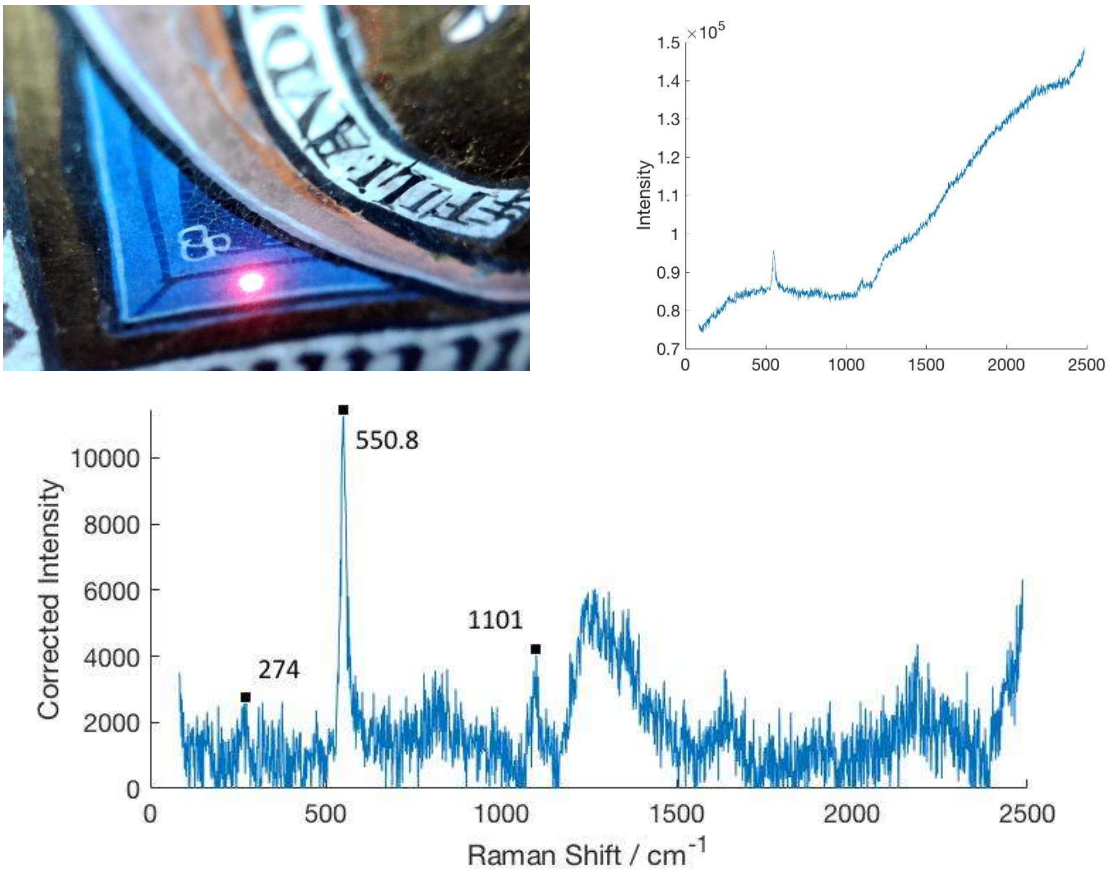


Figure 48: (top left) The area of NCO MS 20 fol. 1 r examined, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

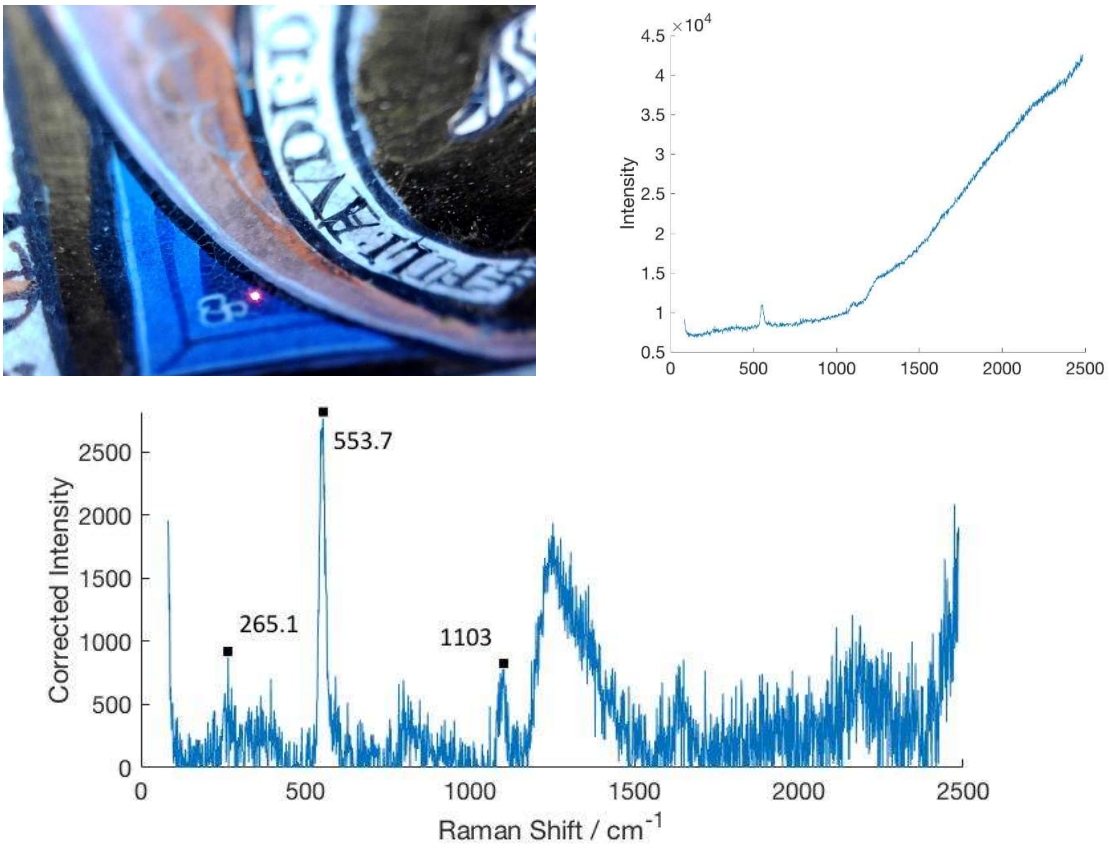


Figure 49: (top left) The area of NCO MS 20 fol. 1 r examined, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

Figure 50 shows the initial on fol. 63v again, which also displays a range of shades of blue in both the drawing inside the initial and in the initial itself. A lighter blue from the initial column and a darker blue from the cloak were examined and found to be lapis lazuli, as seen in Figure 51 and Figure 52 below. Again, both of the spectra obtained from these blues contain fluorescence, which could be due to the binder used.

Figure 50: The initial on NCO MS 20 fol. 65v.

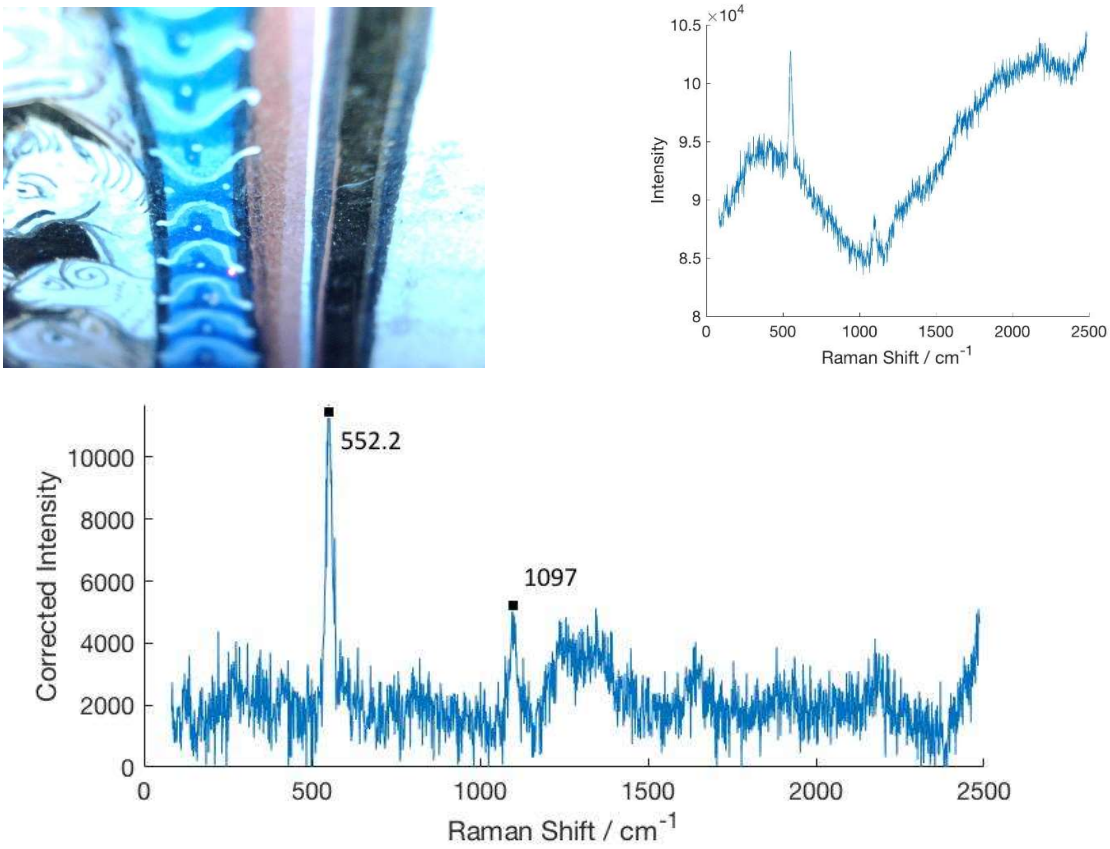


Figure 51: (top left) The area of NCO MS 20 fol. 63 v examined, (top right) the raw spectrum obtained, and (bottom) the processed spectrum.

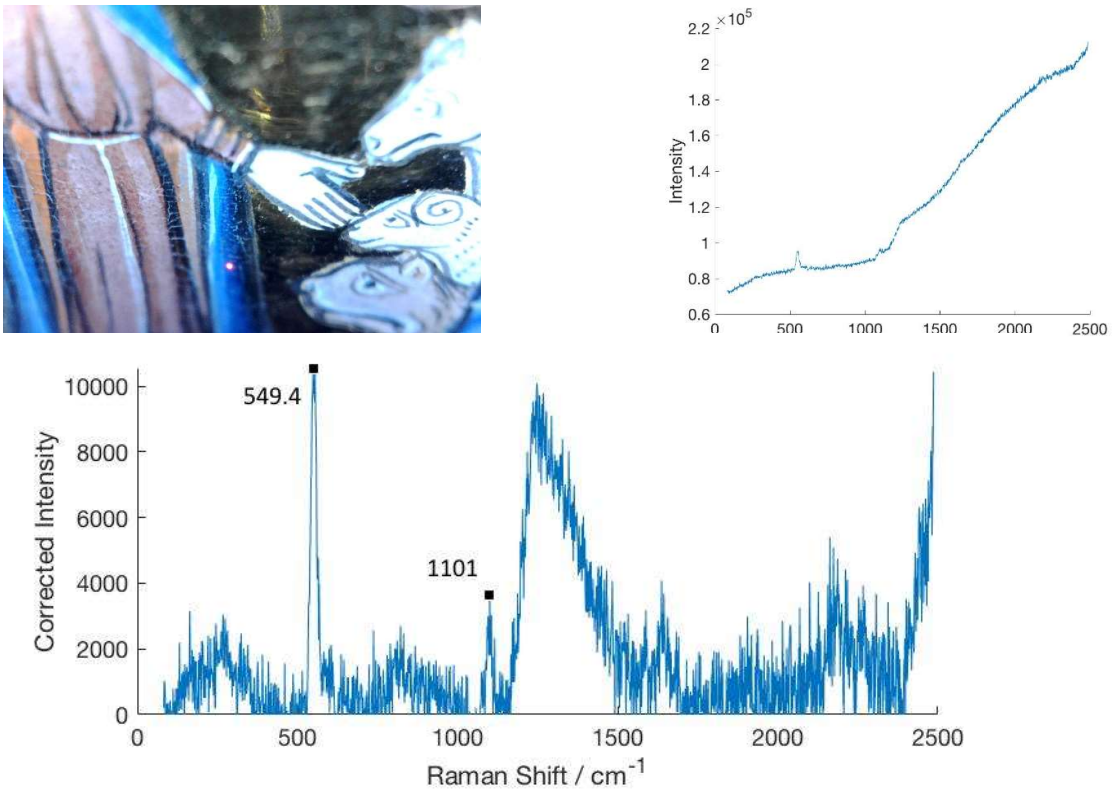


Figure 52: (top left) The area of NCO MS 20 fol. 63v examined (top right) the raw spectrum obtained and (bottom) the processed spectrum.

Figure 53: False colour image of NCO MS 20 fol. 1r.

The false colour image of fol. 1r seen above, in Figure 53, neatly demonstrates the areas where lapis lazuli and azurite are used. Further information about image processing is in Chapter Three. Lapis lazuli does not absorb the infrared wavelengths and so is seen as pink, clearly showing that this pigment was used in both the artwork inside the initial and in the initial itself. However, azurite absorbs infrared wavelengths and so is seen in the blue paraphs.

Use of Orange

As mentioned above, the vibrant orange colour is deployed only in small quantities in the manuscript to colour small objects in drawings or to highlight small details. The colour of the orange suggests that the pigment used is red lead, as this has been the case for similar colours in other manuscripts examined so far in this study. The orange owl on fol. 63v, as seen most clearly in Figure 50, was examined by Raman spectroscopy with the results shown in Figure 54. Although present, the peaks in the raw spectrum at 121 and 565 cm^{-1} are not at all clear, being masked by fluorescence. Even when processed, the peaks, now at 129 and 568 cm^{-1}, are not decisive. (The phenomenon whereby processing changes the position of the peaks is discussed in Chapter Two). In published work, the Raman peaks for red lead are given at 121 and 549 cm^{-1}. [25]

[25] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

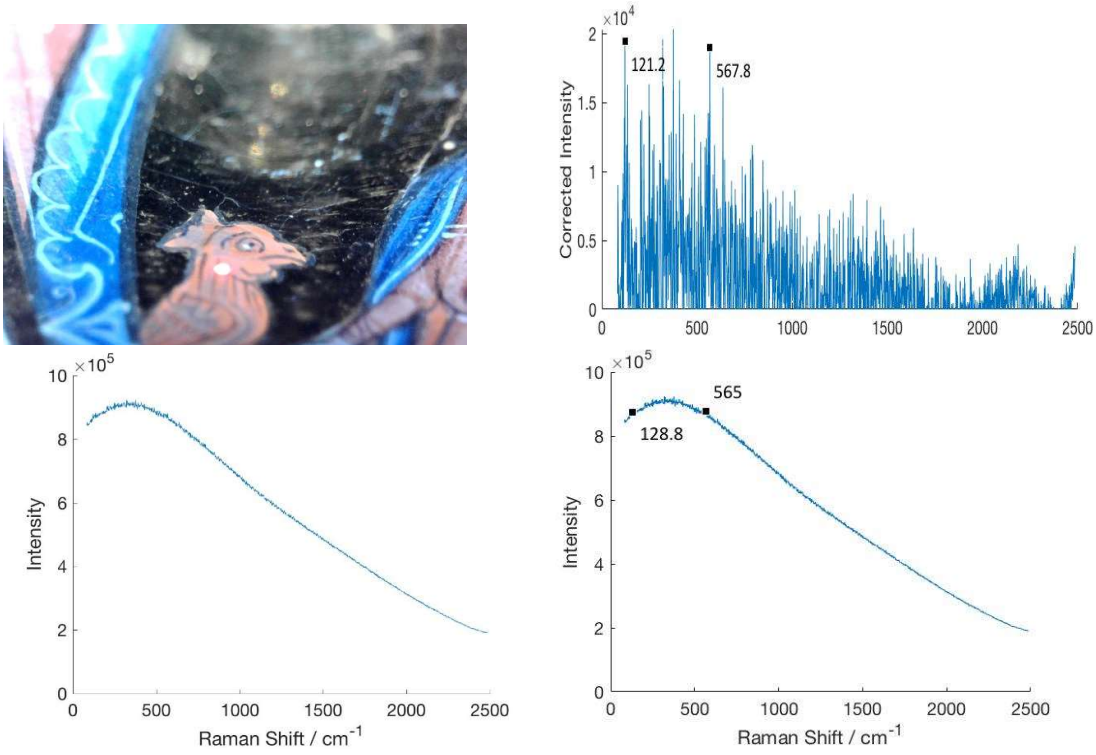


Figure 54: (top left) The spot on fol. 65 r of NCO MS 20 examined, (top right) the processed spectrum, (bottom left) the raw spectrum, and (bottom right) the labelled raw spectrum.

Further examination, by FORS, was undertaken on the orange owl, with the results shown in Figure 55 below. As seen, the inflection point of the spectrum is at 560 nm, consistent with that given for red lead in published works (at 565 nm).[26]

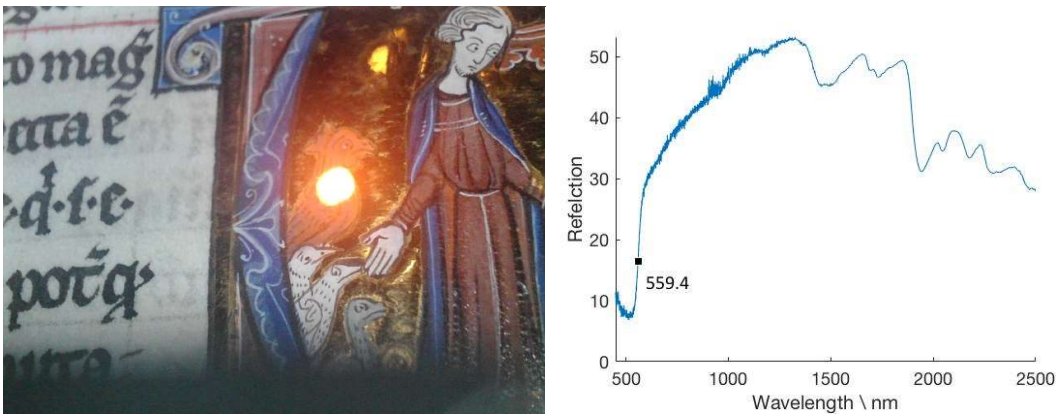


Figure 55: (left) The spot on the initial of fol. 65 v that was examined, and (right) the spectrum obtained.

[26] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

Use of Green

Like orange, green is used sparingly, to colour small objects in drawings or to add detail and is not used for colouring ground or in the wider decorative scheme. An example of its application can be seen in Figure 56 below, where a sweep of green adds a little colour to the white building at the bottom of the scene, and also to the church held by Ecclesia.

Figure 56: NCO MS 20, Cantica (fol. number not recorded).

The green bird on fol. 63 v (who can be seen in Figure 50 above) was examined by FORS, as shown in Figure 57, and found to have an absorbance maximum of 710 nm, which is consistent with that given for verdigris, a copper green, in published works where it is reported at 720 nm. [27]

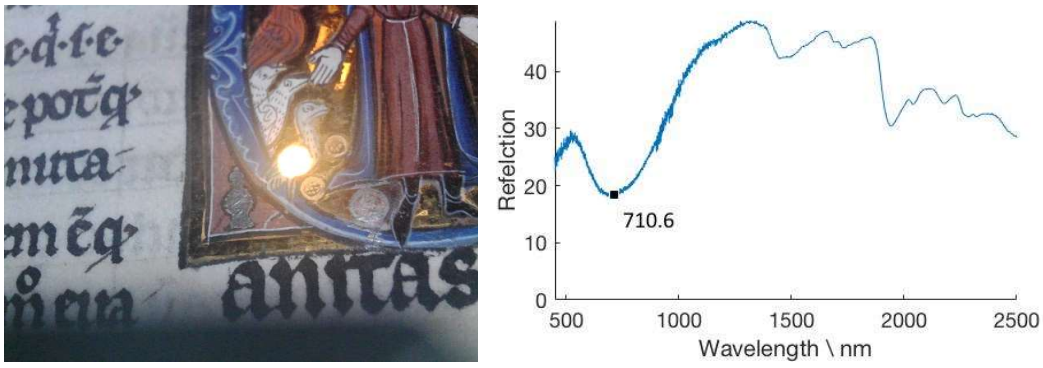


Figure 57: (left) The spot on fol. 63 v examined by FORS, and (right) the spectrum obtained.

[27] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

The green of the bird was also examined by Raman spectroscopy, as seen in Figure 58, below. In the raw spectrum, two peaks at 107 and 1057 cm^{-1} are slightly visible, and these are a little enhanced in the processed spectrum. These peaks are consistent with those given in published data for white lead.[28] The broad peak centring on 500 cm^{-1} is an artefact of the system visible when the laser power is being absorbed, as is the case here, as copper green pigments absorb the laser light at the 633 nm frequency.

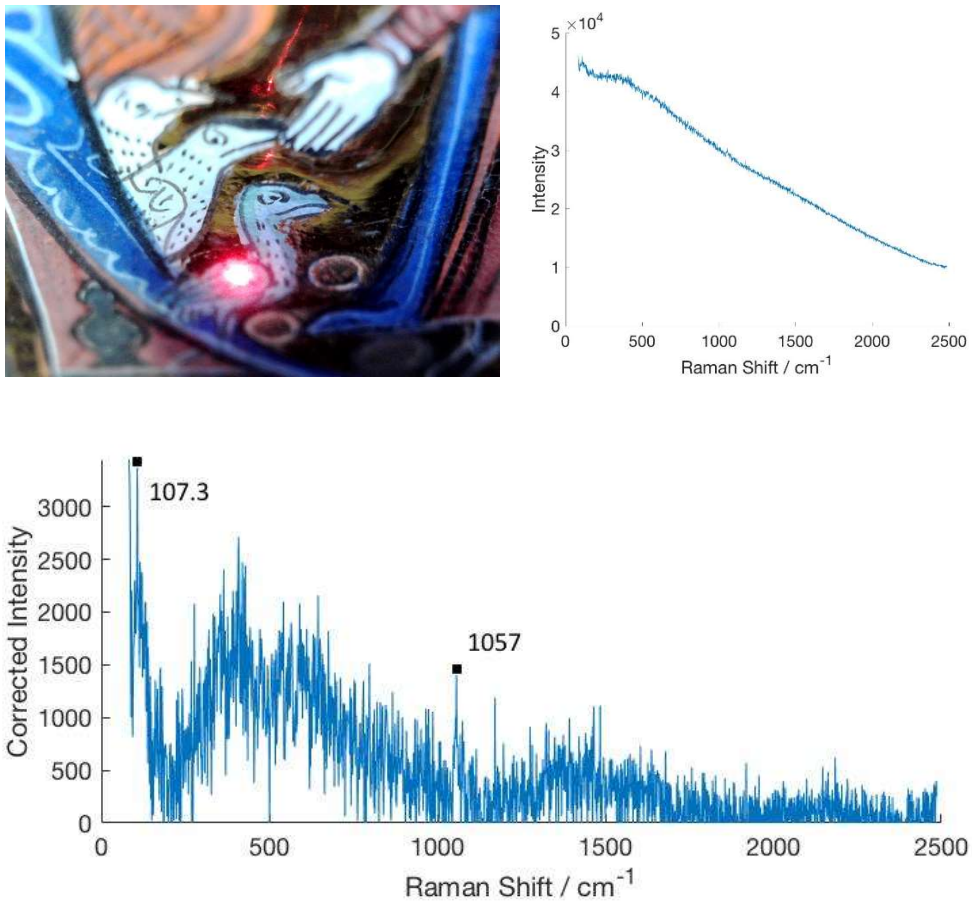


Figure 58: (top left) The spot on fol. 65 r of NCO MS 20 examined, (top right) the raw spectrum, and (bottom right) the processed spectrum.

Combining the information gleaned from the Raman spectrometer and the FORS system indicates that the green is copper-based, probably verdigris, and that there is some white lead present either in the paint itself (close examination of the green bird does show that the green is a paler colour than one might expect for verdigris) or as an undercoat. The latter would not be unusual - white was

[28] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

often used as a background colour to provide hiding power to cover the parchment for paler pigments or, as more likely in this case, to provide a lightening effect. In addition, white lead is the colour with which the other animals are painted (see the section on the use of white, below). An added consideration is that copper green pigments are detrimental to parchment - given time the pigment 'eats' into the parchment - and therefore, it may be that white lead is applied here as a barrier to prevent the parchment from potential erosion.

Use of black

Black was used in the manuscript chiefly for outlines but also occasionally for colouring small objects. On fol. 1 r, the black shoe was examined by Raman spectroscopy and found to be carbon - evidenced by Figure 59.In the raw spectrum, the peaks given for carbon in published data, at 1333 and 1585 cm^{-1}, can barely be seen.[29] However, in the processed spectrum, they are a little clearer - at 1324 and 1579 cm^{-1}.

[29] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p.1222.

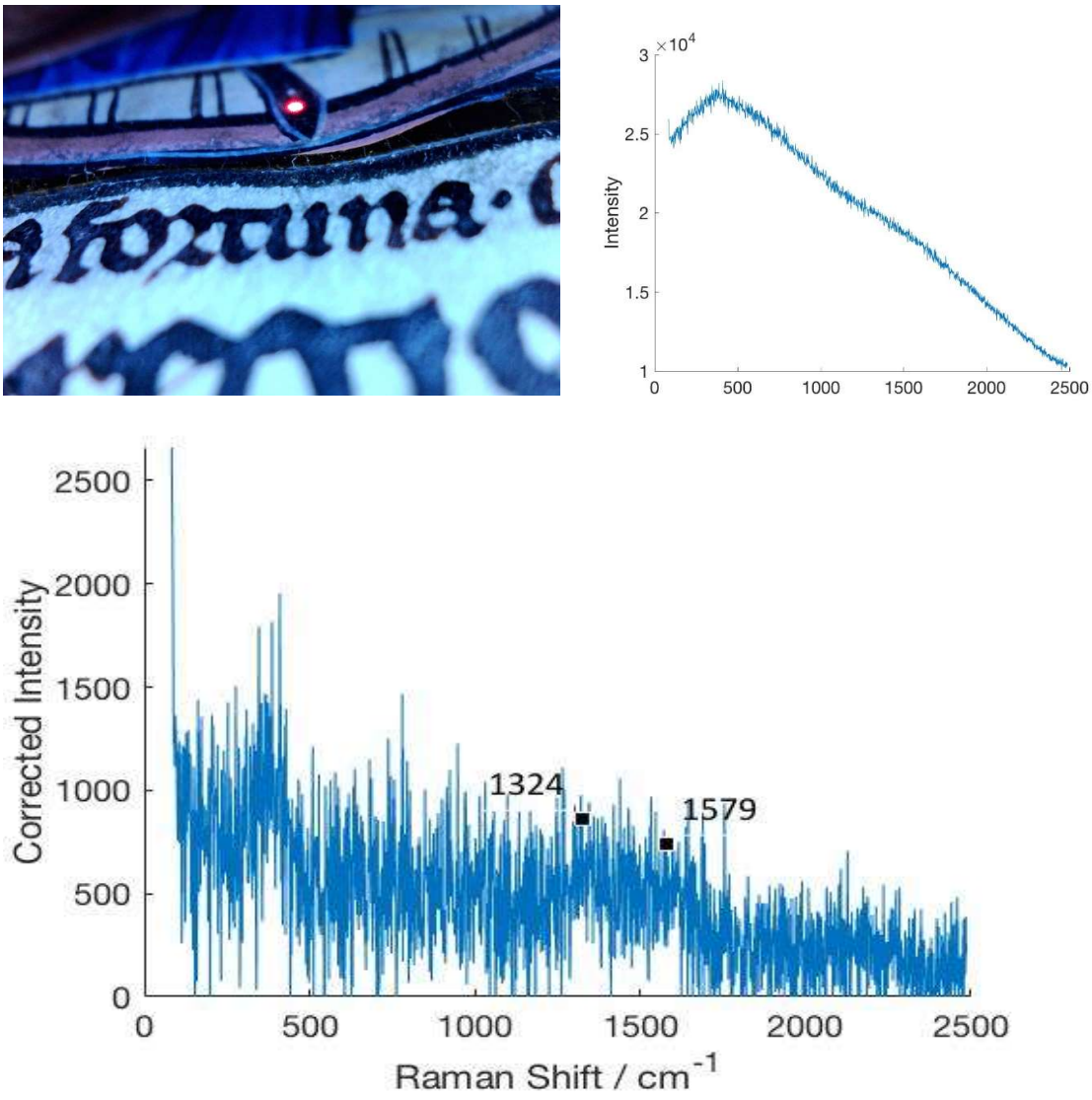


Figure 59: (top left) The spot on fol. 1 r of NCO MS 20 examined, (top right) the raw spectrum, and (bottom right) the processed spectrum.

Further evidence that the black pigment is indeed carbon can be seen in the FORS spectrum acquired from the same area and shown in Figure 60 below. Here, the featureless spectrum with low reflectance, particularly in the visible region, is indicative of carbon.

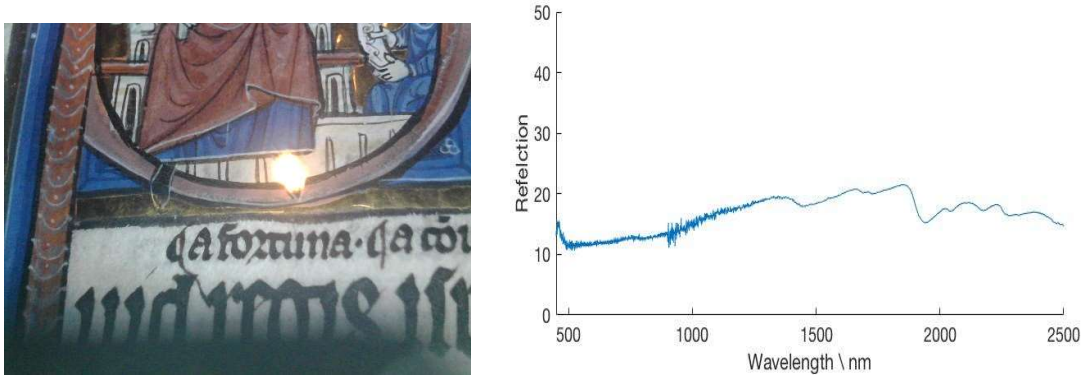


Figure 60: (left) The spot on fol. 63 v examined by FORS, and (right) the spectrum obtained.

Use of pink

Pink is a common colour in NCO MS 20, used to colour both large areas of drawings, particularly for clothing, and as an infill. A pink area on fol. 1r was examined with Raman spectroscopy, and the results are shown below in Figure 61. As both the raw and processed spectra show, there is nothing but fluorescence - a sign that the pink colour is likely made entirely from, or contains, organic material.

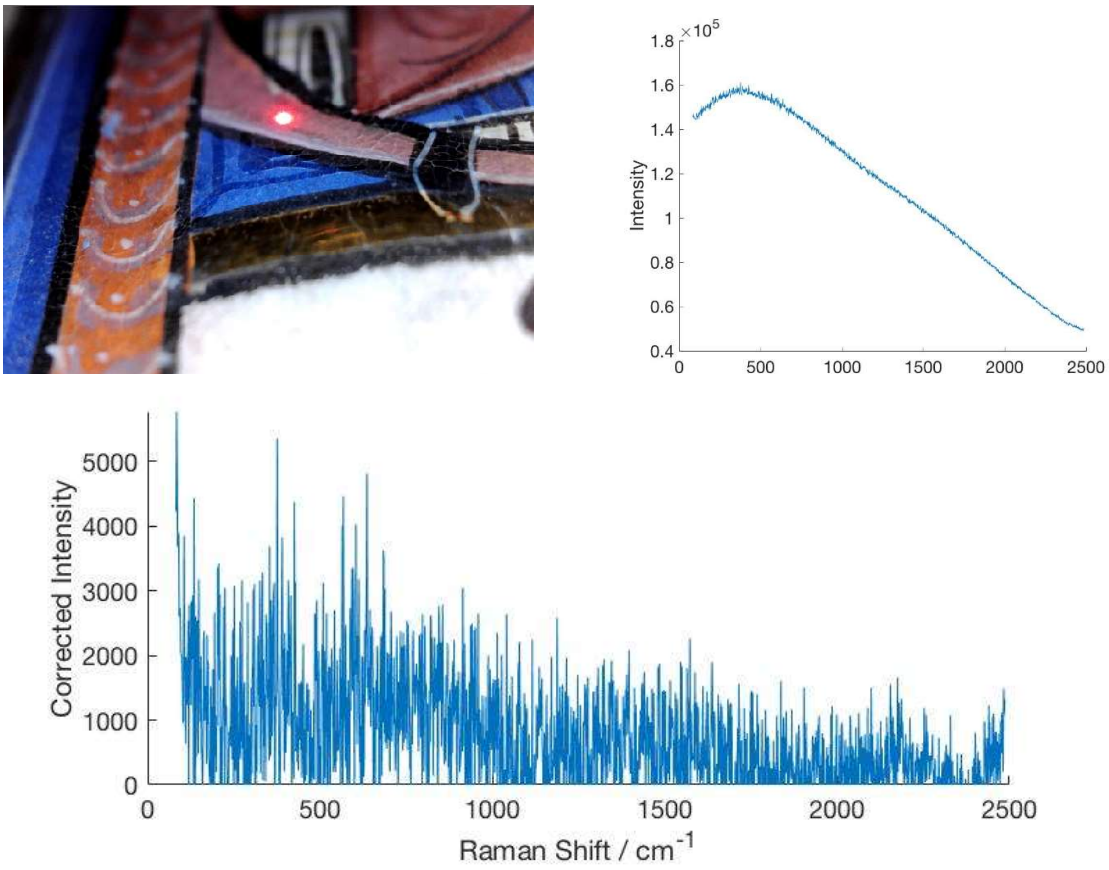


Figure 61: (top left) The spot on fol. 1 r of NCO MS 20 examined, (top right) the raw spectrum, and (bottom right) the processed spectrum.

The pink colour was further examined with FORS, and the spectra obtained are shown in Figure 62 below. Here the inflection point at 593 nm is consistent with that for vermilion, a red pigment, reported in published work as being at 600 nm.[30] However, it would be unusual for vermilion to be present and for it not to have been picked up by the Raman spectrometer, as it usually gives a strong signal. A logical deduction would therefore be that the pink contains some organic substance that gives a similar profile to vermilion when examined with FORS - after all, red and pink dyes will show some feature in the red part of the spectrum - which encompasses 600 nm.

[30] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', p. 1491.

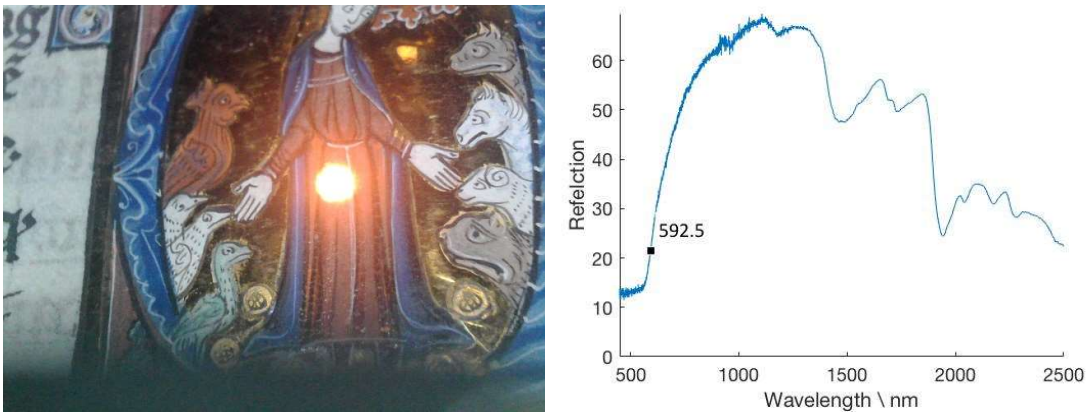


Figure 62: (left) The spot on fol. 63 v examined by FORS, and (right) the spectrum obtained.

Use of white

White is employed regularly in the manuscript both as a colour to modify other colours and in its own right. When used in conjunction with other colours it can be deployed as a highlight, as seen skilfully used in Figure 50 above, or can be seen underneath other colours to provide a base colour on which to work. It may also be mixed in with other colours; in these cases, the white lead produces a lightening effect (as seen in the discussion of green above). Where it is employed on its own is often used for flesh - hands and faces of humans, and also for animals.

The white on fol. 1r and fol. 63v was examined by Raman spectroscopy and by FORS, as shown in Figure 63 and Figure 64 below. No peaks were seen in the raw spectrum or the processed spectrum from the Raman system. The FORS system, however, returned a spectrum consistent with that for white lead with an absorption band at 1443 nm.[31]

[31] John K. Delaney et al., 'Visible and Infrared Imaging Spectroscopy of Paintings and Improved Reflectography', *Heritage Science* 4, no. 1 (16 March 2016), p. 97.

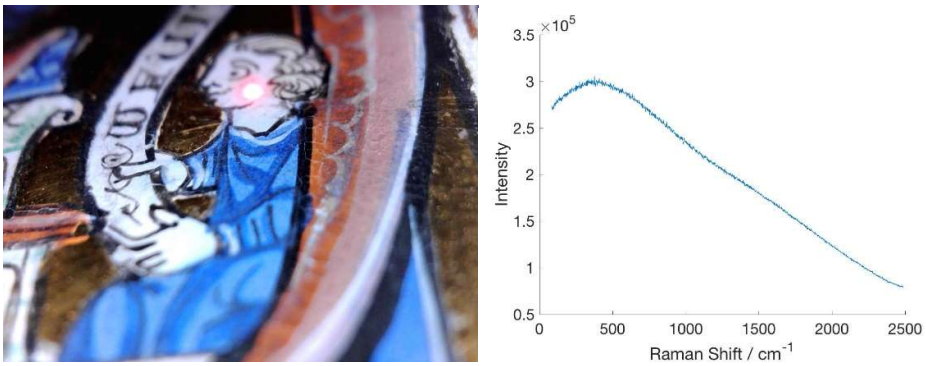


Figure 63: (left) The spot on fol. 1 r of NCO MS 20 examined with the Raman system and, (right) the raw spectrum obtained.

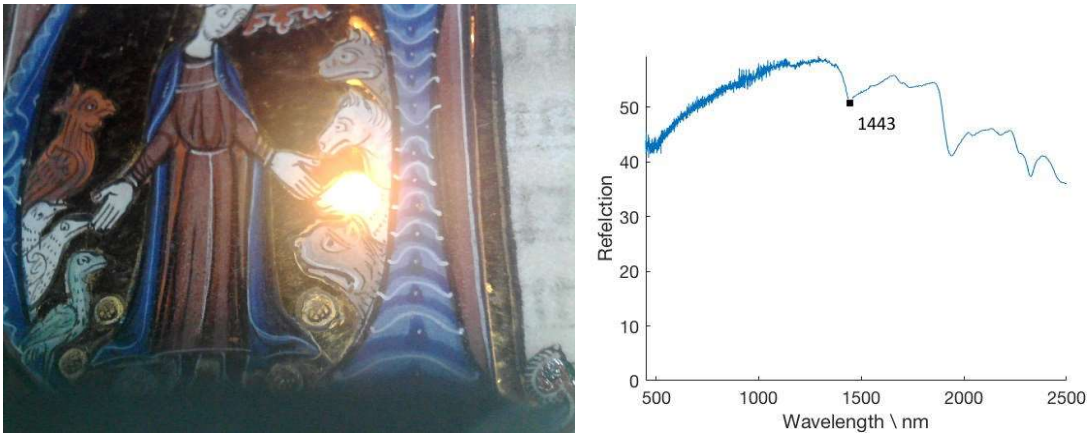


Figure 64: (left) The spot on fol. 63 v examined by FORS, and (right) the spectrum obtained.

Use of yellow

As seen below in Figure 65, at the top left of the initial are two very small areas of pale-yellow decoration. Seen more clearly in Figure 66, this yellow colourant was examined by Raman spectroscopy. However, it did not return a spectrum with any discernible peaks, either in the raw spectrum shown, or in the processed spectrum. The area was too small (and 'contaminated' by other detailing) to yield a FORS spectrum.

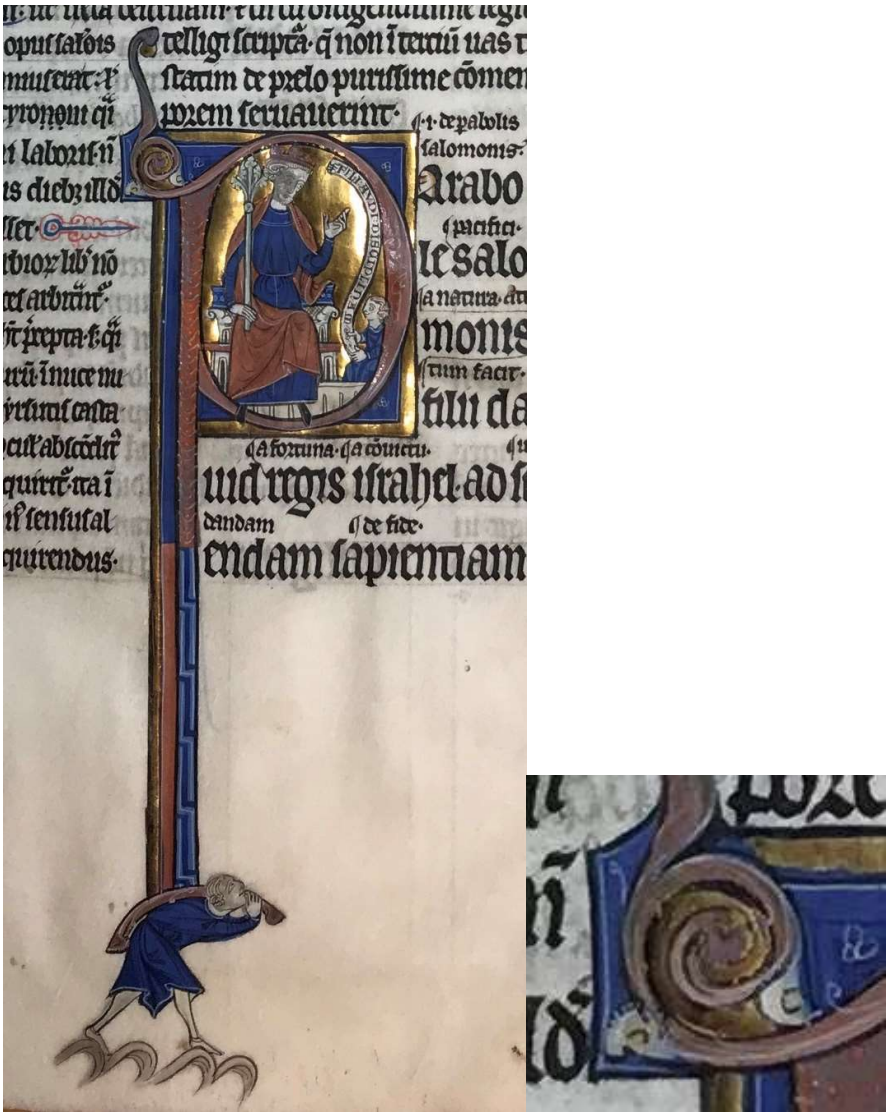


Figure 65: The initial on NCO MS 20 fol. 1 r in full (left), and (right) an enlargement of the tiny yellow areas inside the white.

This colour is likely to be an organic yellow of some sort, possibly weld or saffron, and is applied as a wash over a white substrate, probably white lead (as discussed above). The absence of a white lead spectrum is not unusual, as white lead can be difficult to obtain a clear spectrum from. The absence of any other peaks suggests that orpiment or lead-tin yellow (both yellow mineral pigments) were not employed.

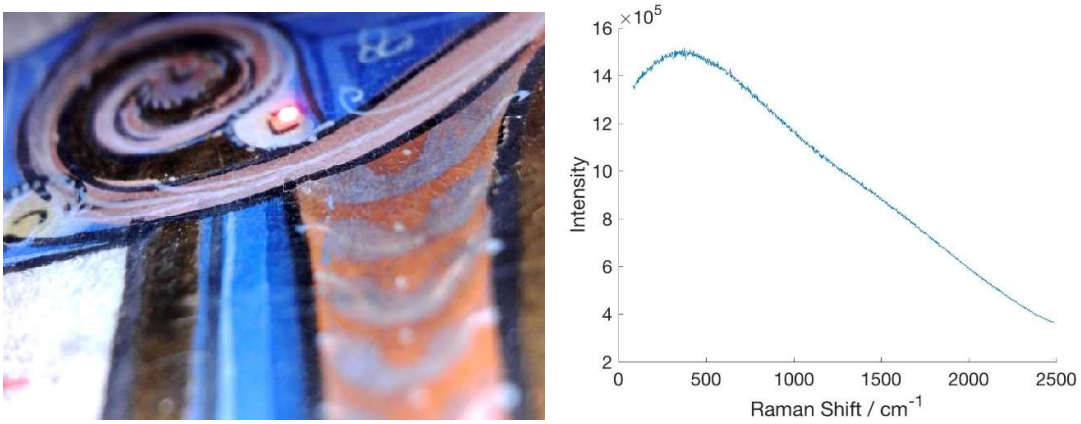


Figure 66: (left) The spot on fol. 1 r where the yellow pigment was examined, and (right) the raw spectrum obtained.

Use of gold

As can be seen most clearly in the full-page images of fols. 1r and 63v below, in Figure 67, much use has been made of gold as the ground to the initials. The gold is lustrous, having been burnished and polished, and has been tooled in places.

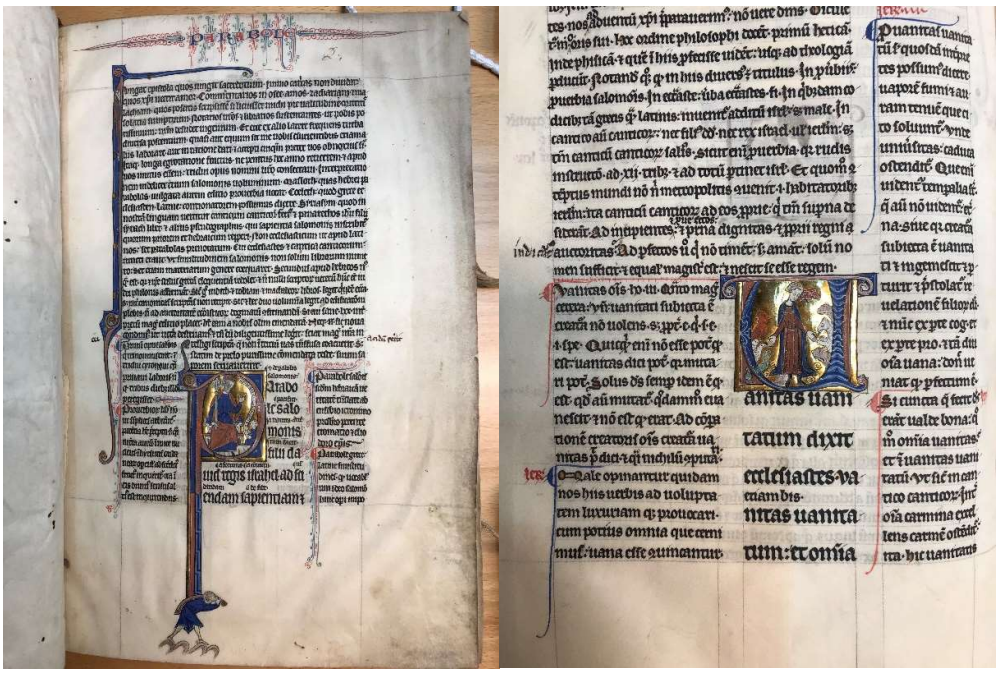


Figure 67: (left) Fol. 1r in full, and (right) fol. 63v in full.

Text and text ornamentation

Text

The text in NCO MS 20 is uniformly black to the eye, but interestingly displays different shades of black when viewed in the infrared above 850 nm. As Figure 68 below shows, the writing immediately underneath the historiated initial appears darker than the surrounding text under infrared light. In the surrounding text there are some parts which have darker shades of ink that can be seen easily under infrared, and those which are barely visible (immediately above the initial, for example).

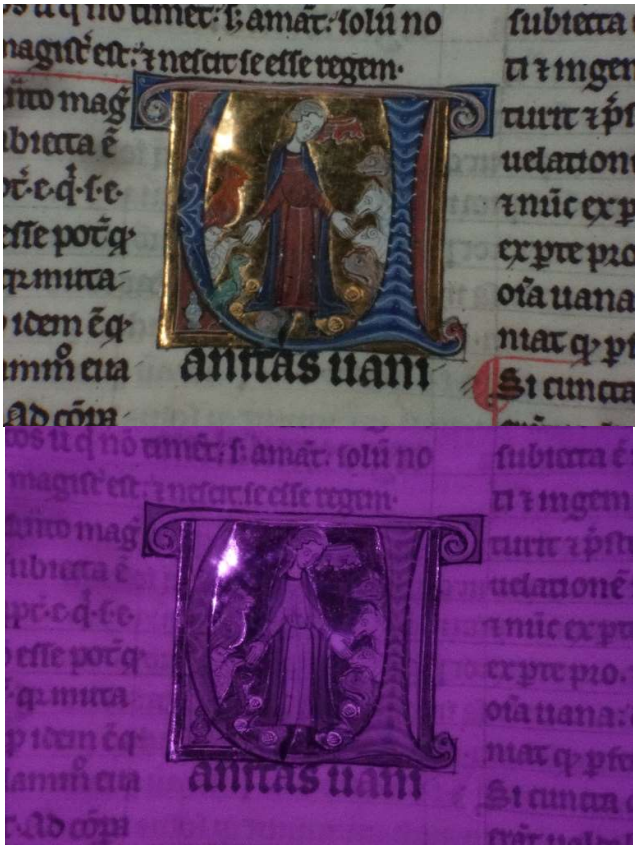


Figure 68: (top) The initial from NCO MS 20 fol. 63 v under white light, and (bottom) the same initial under infrared light.

There are two potential explanations for the varieties of shades of ink. First, that such variations are the natural result of the writing process - the first words written after the pen has been dipped with being darker than subsequent ones, which will become gradually lighter as the nib empties of ink - until the pen is re-dipped. Second, is that the text contains carbon - a pigment sometimes included in ink to darken it (as seen in DCL A.II.3). Carbon appears dark under infrared wavelengths, so if carbon were included in the ink, it would appear darker on the page. However, where carbon in ink

has been seen before, the text has appeared more uniformly black, rather than patchy, as is the case in the 'anitas uam" immediately below the miniature as shown in Figure 68.

The results of examining the text in fol. 1 r with Raman spectroscopy are shown below in Figure 69. In the raw spectrum, two very small peaks can be seen which appear only slightly larger in the processed spectrum. The peaks, at 1325 and 1597 cm^{-1}, correspond with published data for carbon.[32]

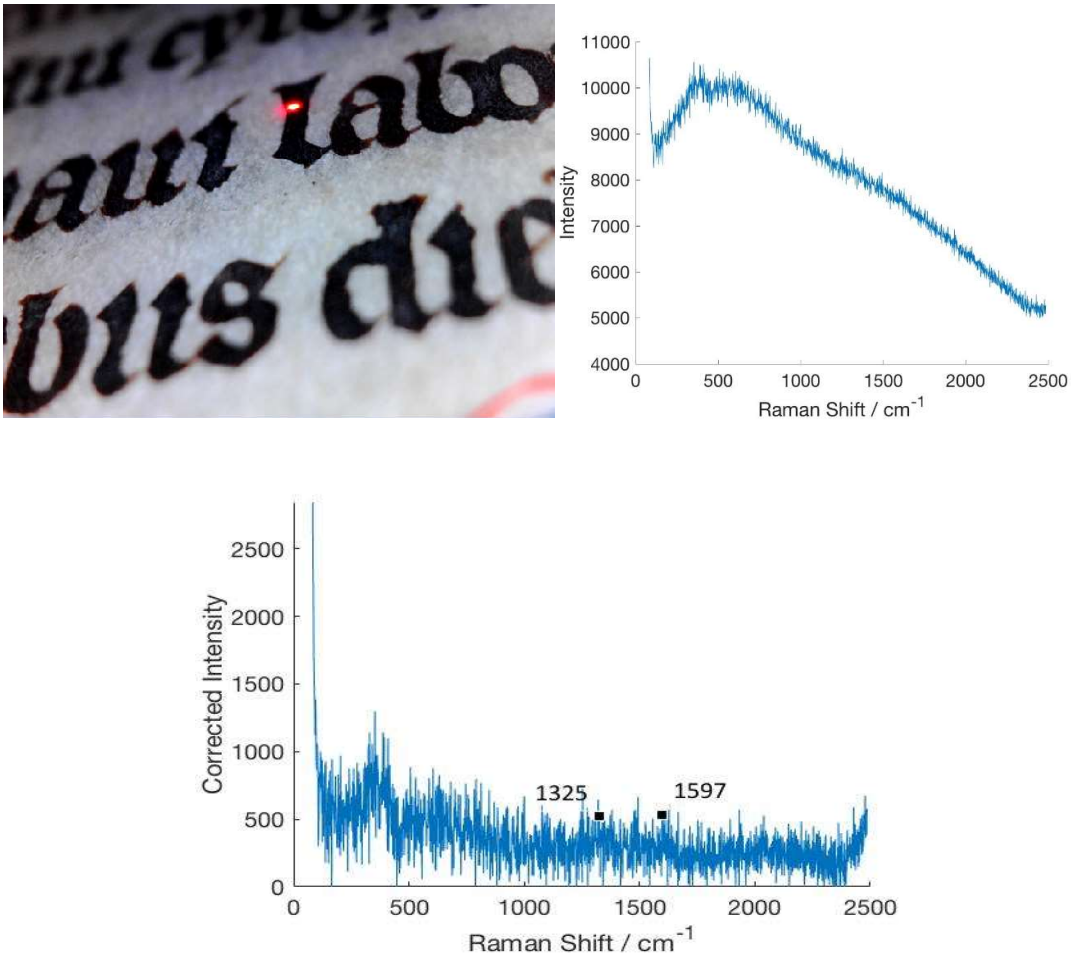


Figure 69:(top left) The spot on fol. 1 r of NCO MS 20 examined, (top right) the raw spectrum, and (bottom right) the processed spectrum.

A FORS examination of the text was also conducted, as seen in Figure 70 below, and this revealed a spectrum that is fairly featureless in the visible range - as discussed above, this is indicative of

[32] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts', p. 1222.

carbon. However, the spectrum has a fairly high reflectance, which is not indicative of carbon - one would expect carbon to reflect very little. The spectrum also has bands in the NIR, which is not typical of a carbon spectrum. It may be that some of the white parchment behind the black letter examined is contributing to the reflectance in the spectrum. Parchment has bands at around 1450 and 1950 nm (seen in the spectrum at 1474 and 1938 nm) that are overtone and combination bands of water. There is also a band at 1730 nm (in the spectrum below at 1734 nm) that is due to the CH group in lipids, whilst the weak band at 2000 nm (here at 2039 nm) is related to the collagen in the parchment.[33]

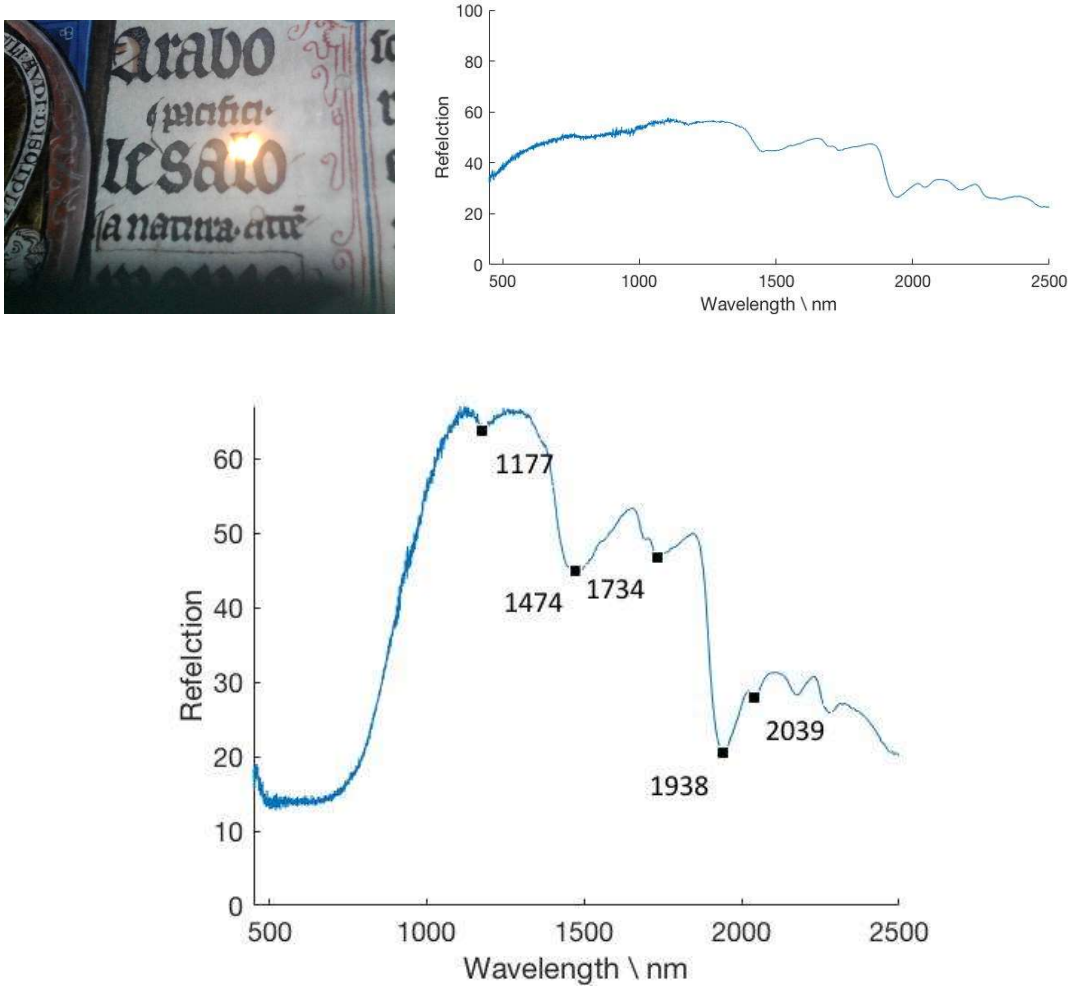


Figure 70: (top left) The spot on fol. 1 r where the black text was examined, (top right) the resulting FORS spectrum unlabelled, and (below) the same spectrum, labelled.

[33] Elena Badea et al., 'Study of Deterioration of Historical Parchments by Various Thermal Analysis Techniques Complemented by SEM, FTIR, UV-Vis-NIR and Unilateral NMR Investigations', *Journal of Thermal Analysis and Calorimetry* 91, no. 1 (January 2008): 17–27.

The infrared image of the fol., seen in below, again shows the patchy nature of the ink. The carbon lines outlining the initial are black in the infrared, and the centre column of text is also approaching black. Most of the text is red, which suggests that the ink does not contain much, if any, carbon. However, that the centre column is slightly darker suggests that this does, and perhaps this was written in different ink and/or at a different time to the rest of the page, as would be expected in a bible gloss.

Figure 71: False colour image of fol. 1r.

Considering both the Raman and FORS evidence as well as the infrared photomicrograph, an argument can be made that the ink in NCO MS 20 does include carbon, in places at least. As carbon in ink is an additive, usually to gallotanic ink at this date, this may account for the Raman and the FORS spectra not being entirely conclusive, as well as the difficult nature of obtaining a FORS spectrum from a letter that does not fill the 'spot'.

Text initials

As seen below in Figure 72 and Figure 73, a flourished text initial on fol. 1 r was examined with FORS. The blue initial returns a spectrum with an absorbance maximum of 637 nm and two absorbance bands at 2285 and 2354 nm characteristic of azurite. Moreover, this seems to be a pure azurite initial, rather than azurite-lapis mix as seen elsewhere in the manuscript, due to the clear bands

present in the infrared section of the spectrum, and the fact that the absorbance maximum is almost exactly as expected for azurite (published data has the maximum at 640 nm). [34]

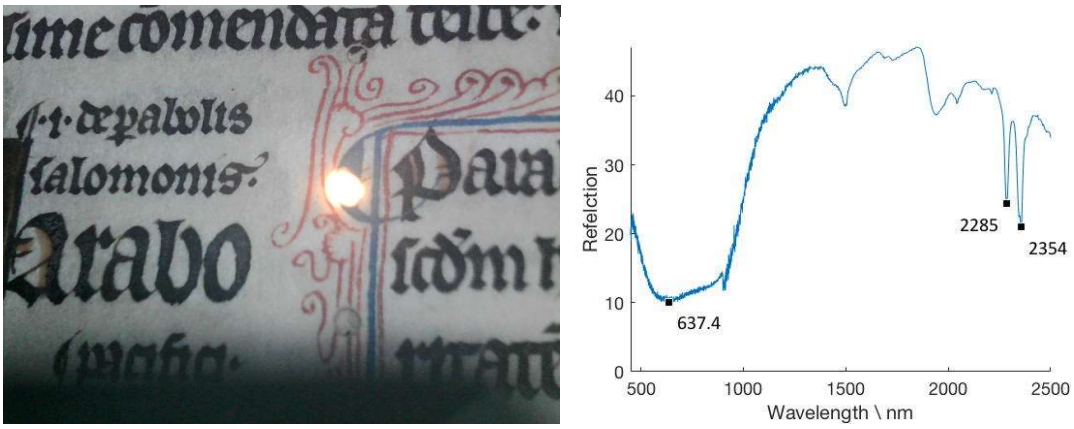


Figure 72: (left) The spot on fol. 1 r examined, and (right) the spectrum obtained.

The red flourishing surrounding the initial was examined and found to have an inflection point of 603 nm, consistent with that for vermilion (at 600 nm in published data.)[35]

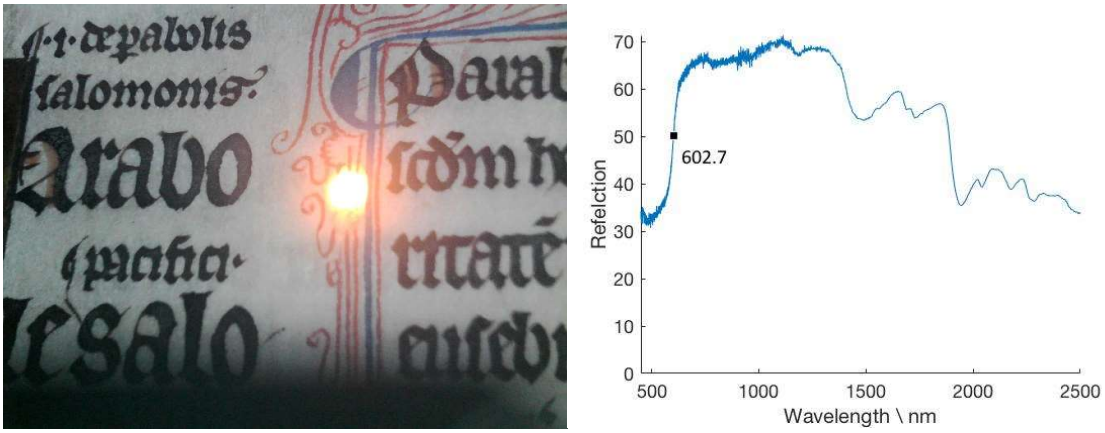


Figure 73: (left) The spot on fol. 1 r examined, and (right) the spectrum obtained.

A blood-red paraph on the same page was examined with Raman spectroscopy and also found to be vermilion, as evidenced in Figure 74 below. Here, the spectrum returns peaks in the processed

[34] Mulholland et al., 'Identifying Eighteenth Century Pigments at the Bodleian Library Using in Situ Raman Spectroscopy, XRF and Hyperspectral Imaging' p. 11; Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry'.

[35] Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry'.

spectrum at 258 and 354 cm^{-1}, consistent with published data that report peaks at 251 and 342 cm^{-1}.[36]

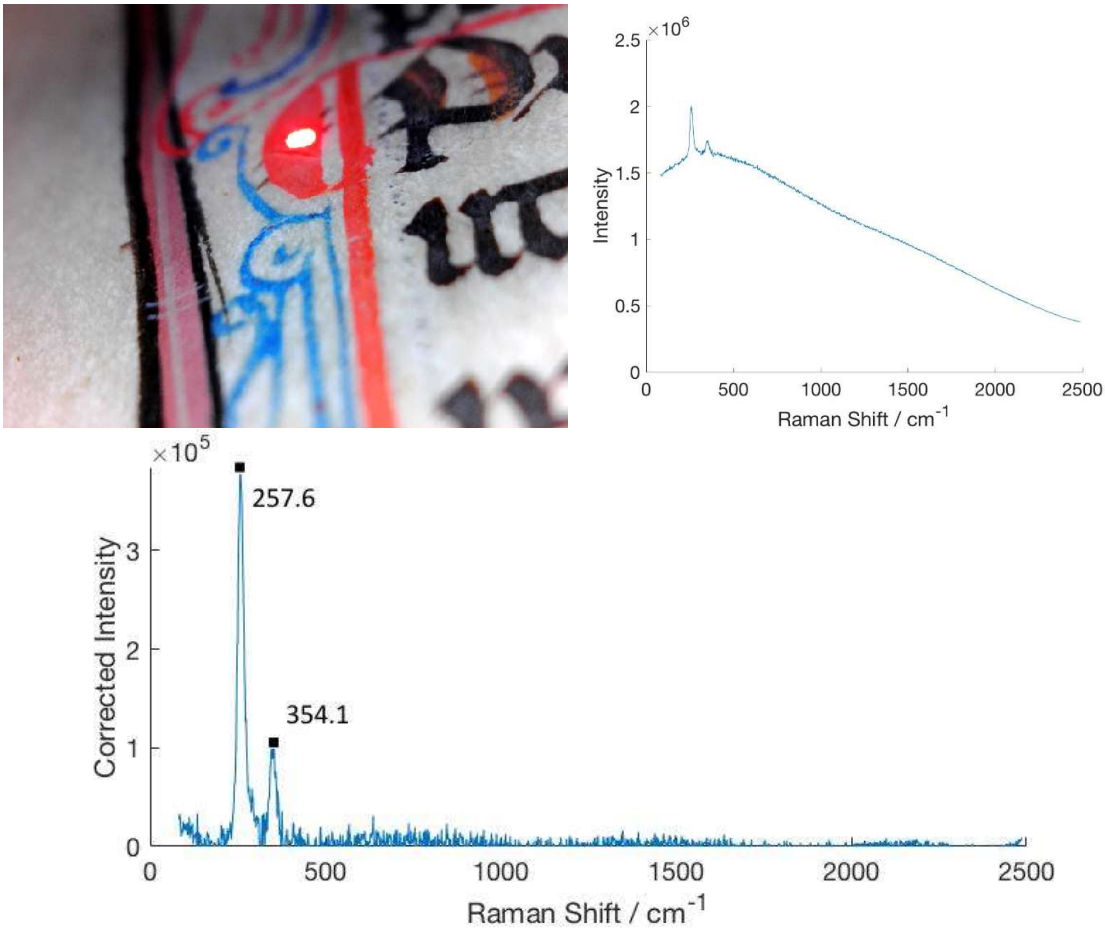


Figure 74: (top left) The spot on fol. 1 r of NCO MS 20 examined, (top right) the raw spectrum, and (bottom right) the processed spectrum.

Interestingly, an orange stroke that highlights a capital, on the same page as the blood-red paraph above, was also found to be vermilion, as shown in below in Figure 75.

That the same pigment is seen in two quite different colours - here a blood-red and an orange - is not unusual. In this case, the difference in colours could either be attributed to the natural variation in cinnabar, the rock from which vermilion is extracted, or from preparation methods changing the colour of the pigment, or from the nature of the binder. Here, the orange vermilion returns a spectrum where the peaks are barely visible through the fluorescence, certainly in comparison to

[36] Marucci et al., 'Raman Spectroscopic Library of Medieval Pigments Collected with Five Different Wavelengths for Investigation of Illuminated Manuscripts'.

the very strong peaks obtained from the more vibrant vermilion. This suggests that the vermilion in the orange sample is mixed with another substance of organic origin, and/or that the vermilion is present in such a small quantity that the fluorescence of the organic binder overpowers its signal.

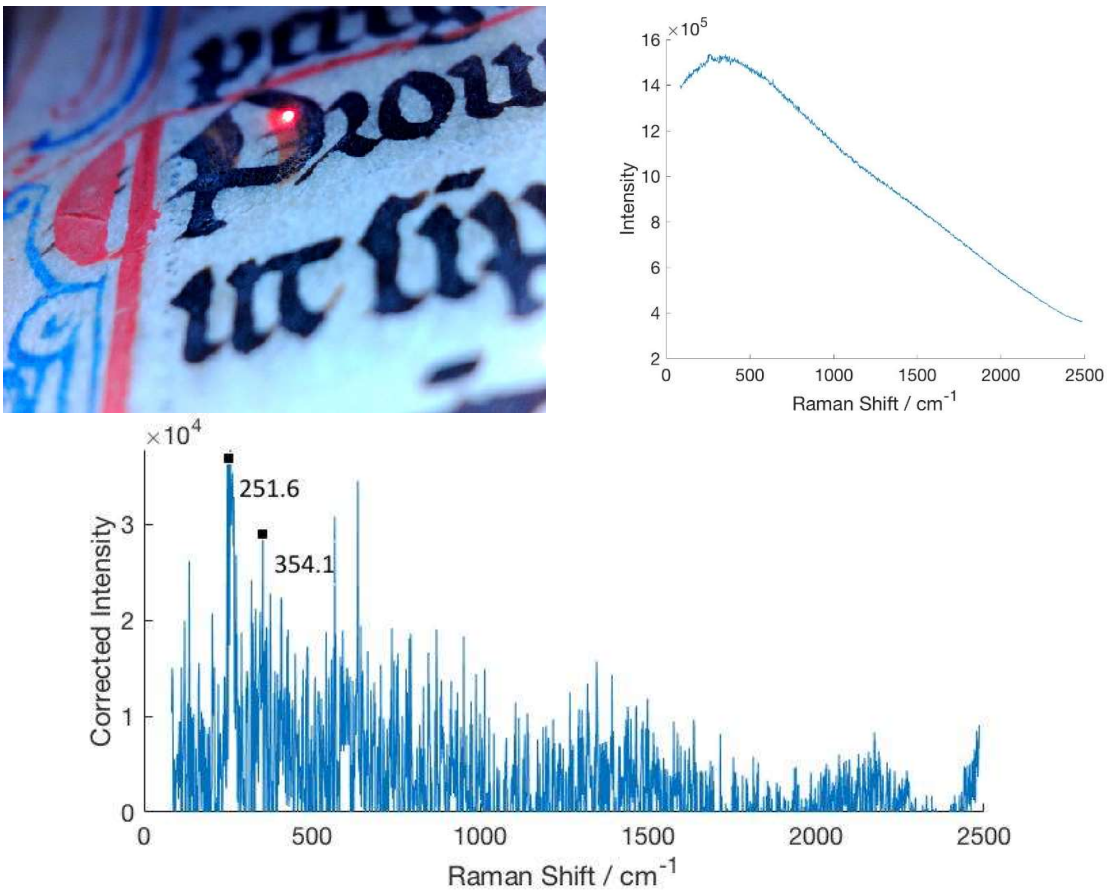


Figure 75: (top left) The spot on fol. 1 r of NCO MS 20 examined, (top right) the raw spectrum, and (bottom right) the processed spectrum.

Further comments on the palette as a whole

Alongside gold, lapis lazuli is the most common pigment seen in the artwork examined in NCO MS 20, sometimes mixed with azurite and sometimes deployed alone. There is also an organic pink, used often, with carbon and white lead similarly regularly employed. Less common colourstuffs used in this manuscript include red lead for orange, and verdigris for green. A tiny amount of what is likely to be organic yellow was seen. Vermilion and azurite were the pigments of choice for text ornamentation, with vermilion employed in both in its usual blood-red form, and in an orange colour. In some areas, carbon may have been added to blacken the oak gall ink.

The application of the expensive pigment lapis lazuli along with gold, alongside the exquisite nature of the artwork and the beautiful script, all contribute to the notion that this is a high-grade manuscript.

All the pigments deployed are commonly seen in manuscripts of this nature made in Southern England in the 13th century, as detailed in chapter two, and as expanded on in the overall conclusion at the end of this chapter.

Colour Analysis of Pink and Blue in All Seven Manuscripts

As seen in the previous sections, all seven of the manuscripts examined contain an organic pink. This was tentatively identified in DCL A.II.3 as a mixture of red and white lead with brazilwood, whilst no diagnostic features were seen in any of the other manuscripts. Further analysis was carried out on this pink colourant as the substance is somewhat omnipresent and yet remains something of a mystery. Aside from the overriding question of what exactly the component(s) in these colourstuffs are, it would be helpful to know if they are all the same - or if each manuscript displays a different version the pink. Was the pink colourant made *in situ* to a standard recipe that produces a similar colourstuff wherever it is made? Was the pink commercially available in a pre-prepared form?

Using L*a*b* colourspace, the pinks in the seven manuscripts were compared (more details on the theory of L*a*b* can be seen in Chapter Two). As can be seen in Figure 76 to Figure 81 below, an image from each manuscript that contained the pink colour was selected, and the pink in the image isolated.

Figure 76: (left) A close-cropped image of the initial on A.II.3 100 v (Kings), and (right) the colour masking showing the areas of pink isolated.

Figure 77: The initial containing a pink colourant Cosinv.V.17 fol. 239 v, and (right) the colour masking showing the areas of pink isolated.

Figure 78: Cosinv.V.18 fol. 316 r, and (right) the colour masking showing the areas of pink isolated.

Figure 79: A.IV.30 fol. 12 r, and (right) the colour masking showing the areas of pink isolated.

Figure 80: The initial on A.IV.37 fol. 337 r, and (right) the colour masking showing the areas of pink isolated.

Figure 81: The initial from Job, New College Oxford, NCO MS 1 (fol. not recorded), and (right) the colour masking showing the areas of pink isolated.

Figure 82: NCO MS 20, initial on Cantica (fol. unknown).

Next, the pink colour was transformed into L*a*b* colour space and the L* component of the colour was then removed to produce plots with axis a* and b*, as can be seen in Figure 83 below.[37] In essence, the plots are a measurement of each pixel of the pink colour, and removing the L* component negates differences in tone and lighting when the image was captured. As the quality of the image (i.e., the number of pixels captured) differs from image to image, some of the plots have more data than others. DCL A.II.3, for example, has been digitised and returns images with a high number of pixels even when an area is magnified. As each pixel is given an L*a*b* value, this

[37] The MatLab code for this procedure can be seen in Appendix G.

provides a plot with a greater density of points. The paucity of pixels in the images captured by cameras with less resolution leads to the phenomenon whereby the pixels do not quite accurately capture the colour gradients, and so some appear to be 'missing' in the plots - hence the white diagonal stripes.

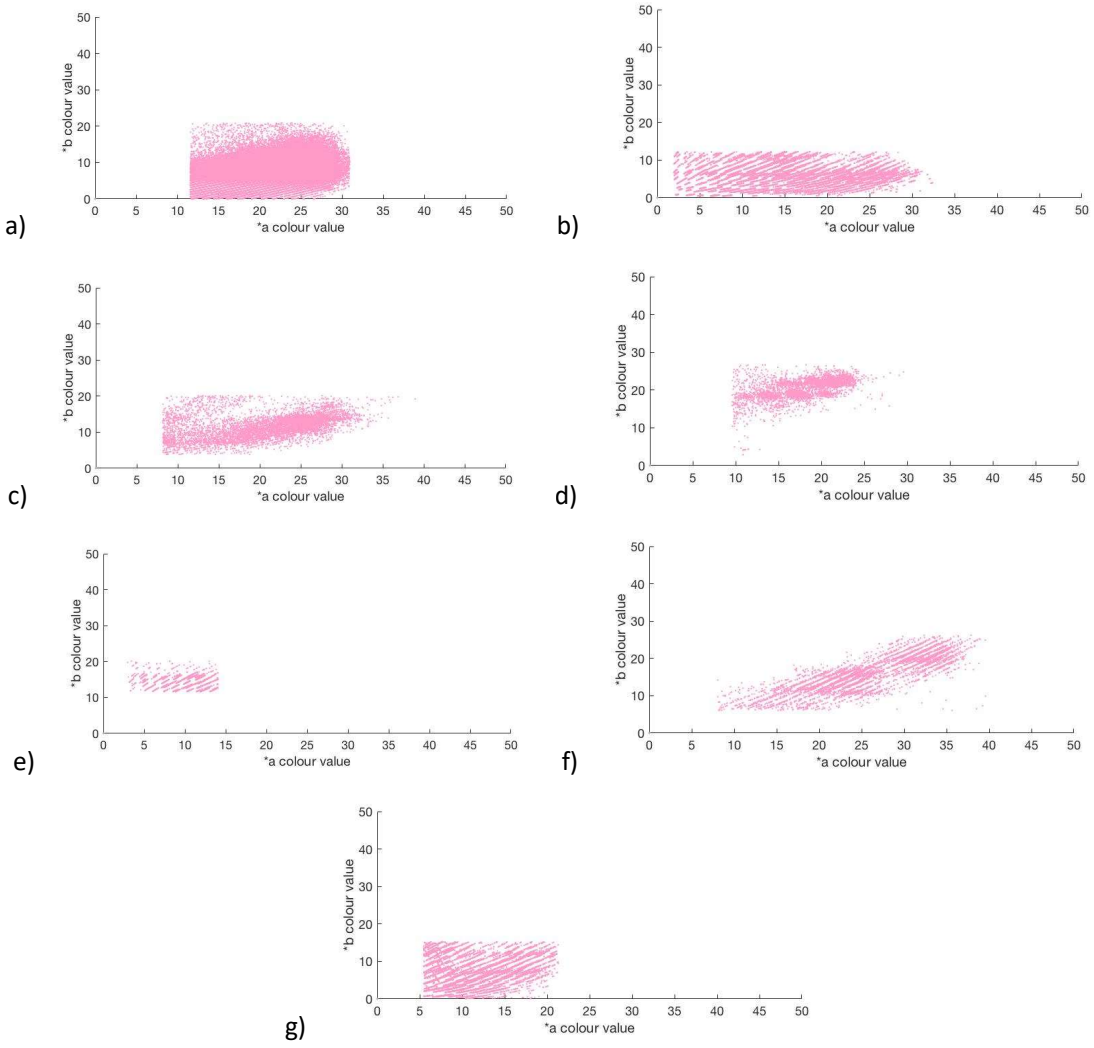


*Figure 83: The a*b* plot of the pink in a) A.II.3, b) Cosinv.v.17, c) Cosinv.v.18, d) A.IV.30. e) A.IV.37, f) NCO MS 1 and g) NCO MS 20*

PINK	Mean a*	Mean b*	Median a*	Median b*
A.II.3	22.2	8.25	21.3	10.4
Cosinv.v.17	16.3	5.7	17.2	6.4
Cosinv.v.18	21.3	11.8	23.6	12
A.IV.30	18.5	20.7	19.6	14.8
A.IV.37	10.6	14.4	8.5	15.9
NCO MS 1	26.0	16.1	23.8	16.2
NCO MS 20	12.3	7.5	13.9	7.7
Mean	18.2	12.06		
Standard deviation	5.1	4.96		

Table 1: The mean and median of the a and b* values from the pinks examined, and the mean and standard deviation of an 'average' pink.*

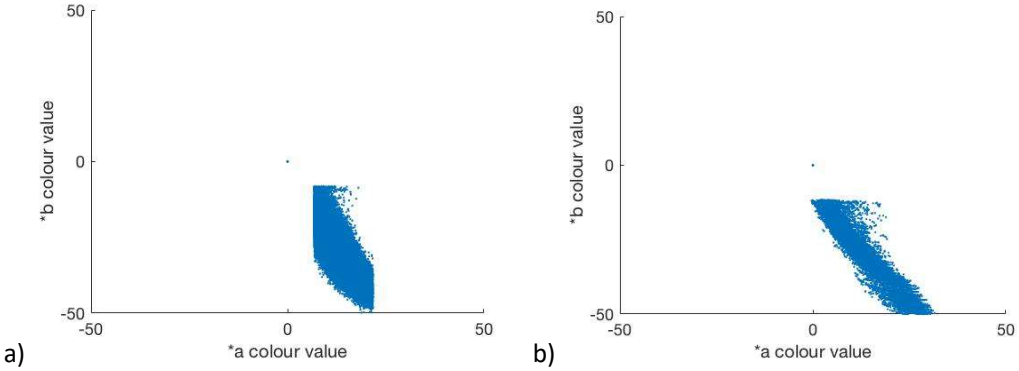
The science of measuring and quantifying colours is vast and complex, and there are many different ways in which the pink colours can be evaluated and compared. The most recently agreed system whereby the CIE L*a*b* values are compared accurately by Euclidean distance in the colourspace takes into account the a* hue rotation that deals with the problematic blue region (whereby blue hues become distorted when viewed from certain angles), in addition to compensating for neutral colours, lightness, hue and chroma.[38] Such an exploration is beyond the scope of this study (and would involve some different methods of data collection and equipment).

However, even at a glance at the plots of the a*b* values shows that whilst the pink colours inhabit broadly the same area of colourspace (as they are all pink), they are all slightly different from each other, as each pink displays quite different values in the pink region of a*b* colourspace.

[38] Gaurav Sharma, Wencheng Wu, and Edul N. Dalal, 'The CIEDE2000 Color-Difference Formula: Implementation Notes, Supplementary Test Data, and Mathematical Observations', *Color Research & Application* 30, no. 1 (February 2005): 21–30.

A closer examination of the plots does reveal that the pinks in DCL A.II.3 and DUL Cosin v.V.18 are very similar - the means and medians are within a few points of each other - but when taken as a whole the difference in values for the collection of pinks does not seem to suggest that they are the same substance. Three manuscripts (DCL A.IV.37, NCO MS 1 and NCO MS 20) fall outside of one standard deviation of the mean for the a* value, and 2 different manuscripts fall outside the standard deviation from the mean for the b* value (DUL Cosin.v.V.17 and DCL A.IV.30), meaning that only two could be said to be a 'standard' pink. Of course, this is only a small sample, but this does suggest that the colourants are not homogenous.

The disparities are underlined when these results are compared with those for the blue (previously identified as lapis lazuli) from the same images. The regions that the blue colours inhabit, when analysed in the same way, correspond much more closely to each other, as can be seen in Figure 84.



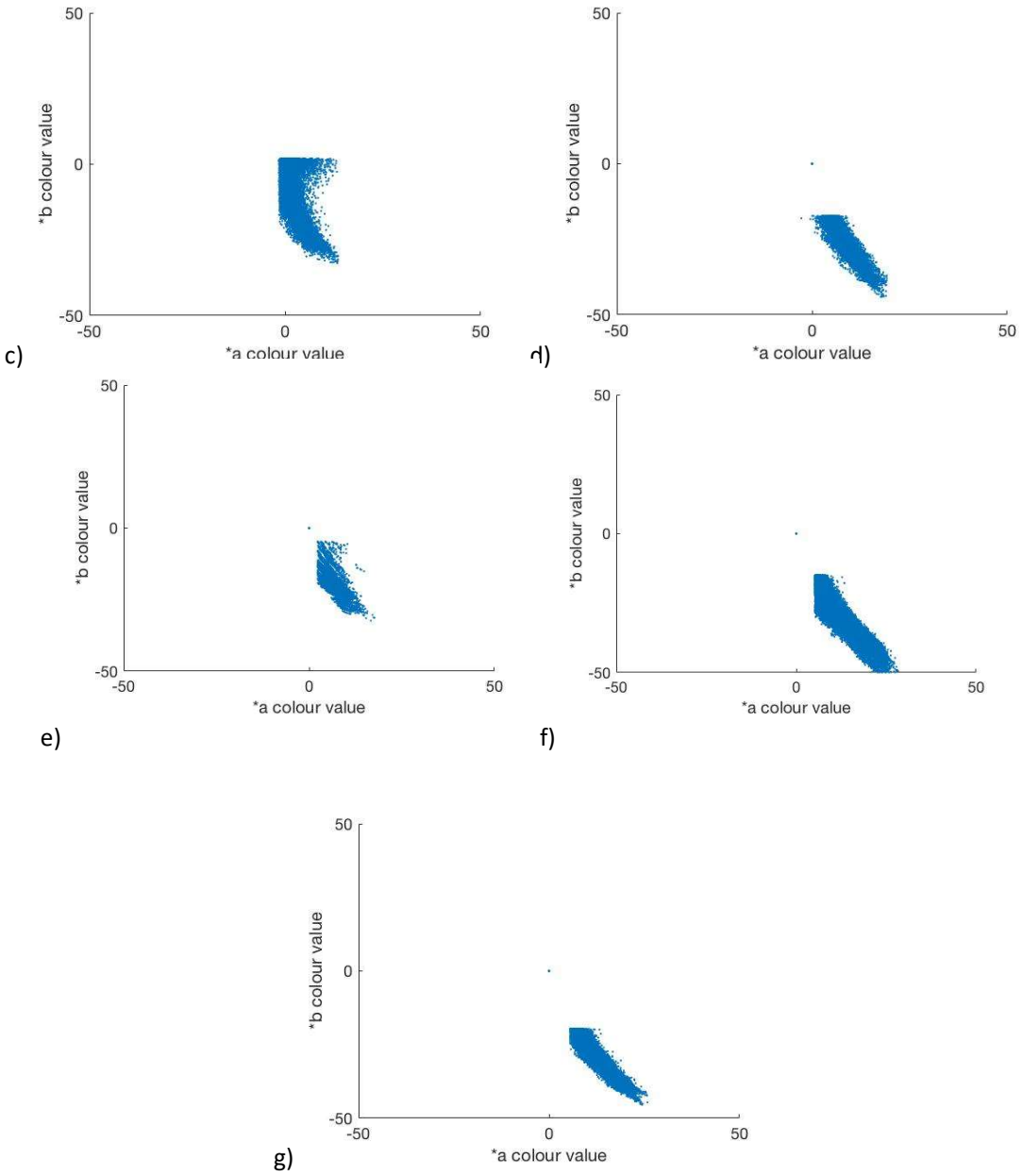


*Figure 84: The a*b* plot of the pink in a) A.II.3, b) Cosinv.v.17, c) Cosinv.v.18, d) A.IV.30. e) A.IV.37, f) NCO MS 1 and g) NCO MS 20.*

The means and medians of the blue a*b* values are closely grouped together, as can be seen in Table 2. Indeed, only one manuscript falls beyond one standard deviation of the mean for the a* value (A.II.3) and two fall outside the standard deviation for the b* value (A.II.3 again, and Cosinv.v.18). All in all, this suggests a much more consistent blue colour across the seven manuscripts. Knowing that this homogenous colour is the same pigment implies that the disparity in the pink colours is due to the colourstuffs not being the same.

BLUE	Mean a*	Mean b*	Median a*	Median b*
A.II.3	2.3	-5.3	10.9	-25.3
Cosinv.v.17	1.6	-3.6	17.1	-27.5
Cosinv.v.18	0.5	-0.4	6.0	-15.4
A.IV.30	0.7	-2.0	8.2	-22.0
A.IV.37	0.5	-0.9	8.8	-16.1
NCO MS 1	1.9	-4.1	16.3	-29.5
NCO MS 20	1.2	-2.8	12.9	-22.7
Mean	1.2	-2.7		
Standard deviation	0.7	1.8		

Table 2: The mean and median of the a and b* values from the blue examined, and the mean and standard deviation of an 'average' blue.*

The differences in the pink colour could be for two reasons, either that the colourstuffs do not have the same components meaning the colours are not homogenous, or that the pinks contain the same colourstuff but one that produces a slightly different colour depending on the method of preparation. What is demonstrated here is further evidence that should one pink be identified, the results cannot be extrapolated to identify a similar colour in another manuscript.

Conclusion

Overview

Seven manuscripts were examined in this study. Four, if not five, were thought to have been made in France, and two in Southern England. Three were pocket-sized bibles, two were larger portable bibles, one was a glossed part-Bible, and one was designed for the lectern. All were produced in the thirteenth century.

Results

Table 3 encapsulates the data collected in this study and presents a list of the pigments that were found in the manuscripts.

	MANUSCRIPTS EXAMINED						
	DCL A.II.3	DUL Cosinv.V.17	DUL Cosinv.V.18	DCL A.IV.30	DCL A.IV.37	NCO MS 1	NCO MS 20
Vermilion	✓	✓	✓	✓	✓	✓	✓
Red lead	✓	✓	✓	✓	✓	✓	✓
Brazilwood		✓*				✓*	
Organic Pink	✓*	✓*	✓*	✓*	✓*	✓*	✓*
Organic Yellow							✓
Orpiment			✓				
Malachite							

	Copper Green	✓	✓	✓	✓	✓	✓	
	Verdigris	✓*		✓*	✓*			✓
	Vergaut *	✓					✓*	
	Lapis Lazuli	✓	✓	✓	✓	✓	✓	✓
	Azurite	✓		✓			✓	✓
	Indigo	✓						
	Organic Purple							
	Folium						✓	
	White lead	✓	✓	✓	✓	✓	✓	✓
	Gypsum		✓					
	Lapis ash	✓			✓	✓	✓	
	Carbon	✓	✓	✓	✓	✓	✓	✓
	Gold	✓	✓		✓	✓		✓
	Mosaic Gold	✓						

*Table 3: A chart of the colourants identified in this study. A tick with a dot denotes a tentative identification. * Vergaut is a green comprised of a yellow and a green colourant. In A.II.3 this is identified as bring lapis lazuli (blue) plus an unidentified yellow. In NCO MS 20 this is very tentatively identified as being lapis lazuli and an unknown yellow – the question remains as to whether the lapis lazuli is contamination of a copper green.*

Discussion of palette

When pigment deployment in all the manuscripts is considered as a whole, patterns emerge. In this section, each colourant is considered in turn, before wider themes are discussed.

Lapis lazuli, although expensive, is seen in all manuscripts whether they are English or French. It is employed extensively too: all of the manuscripts are awash with the vibrant colour. Despite its cost, it was deployed routinely in volumes of different grades – from the opulent DCL A.II.3 to the humbler DUL Cosin Bibles. Patently, the colour it provides was desired by the artists using it. As well as these considerations, more prosaically, the pigment is an easy one to work with - it is inert, does not fade, and is uncomplicated to make into paint and apply to parchment.

In four of the seven manuscripts (DCL A.II.3, A.IV.30, A.IV.37, and NCO MS 1) **lapis ash** is included in the palette. Lapis ash is a low-grade by-product of lapis lazuli extraction, the full details of which, including related recipes for preparation, are found in Chapter Two. It is not known if the lapis lazuli extraction from crude rock, and subsequent preparation into a pigment ready to paint with, was done 'in-house', or in the locale of where the manuscripts were made, or performed close to where the rock was mined in Afghanistan. However, local preparation is unlikely given the time and expertise needed to extract the colour from the rock, the extended trade routes on which it would travel, and the ratio of useful pigment extracted to waste products. However, if the lapis lazuli was extracted locally, then lapis ash would have been an available and cheap by-product of the process. If imported as a pre-prepared powder, then lapis ash would have been more expensive, but no doubt still cheaper than the prized lapis lazuli. Howsoever it was procured, employing lapis ash produced a more attractive grey than carbon and white lead, for example, and its deployment could have been a sign that the illuminators wished to confer a higher status on the book, or simply an aesthetic choice.

As discussed in detail in Chapter Two, lapis lazuli has been seen in European books since c.800 CE. The deployment of lapis lazuli, and lapis ash, in all of these manuscripts, indicates that the pigment was not rare at this juncture, and adds to the weight of evidence that indicates that the trade routes of lapis lazuli, from what is now Afghanistan to the West were still active in the thirteenth century. This abundance is not the case in the middle of the fifteenth century - when lapis lazuli becomes a scarce commodity, certainly in Britain.[39]

What is perhaps surprising is the restrained use of **azurite**; seen in only four of the seven manuscripts. As discussed in Chapter Two, the pigment has been in use since antiquity, and is in frequent use in both France and England in the fourteenth and fifteenth centuries. During the thirteenth century azurite would have been imported from Germany, where it was employed more extensively from the tenth century. Although azurite was clearly available in both France and

[39] Gameson et al., 'Late Medieval English Illuminators' Blues'.

Southern England, as its appearances in DCL A.II.3, DUL Cosinv.v.18, NCO MS 1 and MS. 20 confirm, its sparing use suggests either that supply of the pigment was limited, or that azurite was rejected in favour of the more expensive and higher status lapis lazuli. In England, azurite achieves parity with lapis lazuli in the middle of the thirteenth century.[40]

That azurite should be seen in the most opulent of the manuscripts, A.II.3, suggests that due to its status – a showpiece book intended for the lectern – a wider range of artistic effects was sought – and therefore a more extensive range of pigments than was the norm was employed. When compared to the more limited palette, and reduced number of artistic effects, of the other manuscripts examined in this study, this is certainly the case.

The sparing deployment of **indigo** in this corpus is also unusual. It is seen only in A.II.3, again adding weight to the idea that A.II.3 contains an increased variety of artistry, obtained in part by the deployment of a wider variety of pigments. Considering indigo was an inexpensive pigment, fairly easily obtained (as discussed in Chapter 2), and not difficult for an artist to work with, it is notable that it is not seen more often in the flourishing and pen work where it is typically employed routinely.

Vermilion - another imported pigment that, at this time, is thought to have been sourced from Southern Italy – is identified in all the manuscripts. Appearing at the end of the tenth century, vermillion begins to displace red lead as the standard red in illumination in England and France in the middle of the eleventh century. Its prevalence is likely due to the fact that, again, it is an easy pigment to make into paint and apply, as well as being vibrant and not prone to fading, and is inert in most cases - although it does degrade over time. That it is included in every manuscript examined here is no surprise.

Red lead and **white lead** are both seen in all the manuscripts examined, which is expected given their ubiquity in manuscripts across Europe before and after, not just during the thirteenth century. Both are pigments that are easily manufactured, with white lead the precursor of red lead, and as such were either made on-site where the manuscripts were created, or procured locally. The ease of obtaining these pigments must have been reflected in their price. Additionally, the fact that both pigments are easy to work with and produce paints that give strong colours in a range of hues (that can be mixed if required) make them an obvious choice for use in a wide range of manuscripts, echoed in their inclusion in all the manuscripts examined here.

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[40] As seen, for example, in the de Brailes Hours examined by Team Pigment at New College, Oxford, in 2020.

Carbon is also seen in every manuscript. Again, this was an easy pigment to make or obtain and is easily deployed onto parchment. Its employment in every manuscript here is not unexpected.

The **organic pink** is similarly found in every manuscript, which, if logic applies, means that it too was easily sourced or manufactured, and was easily applied. However, the pink colour is difficult to identify. There is some evidence that the pigment could be brazilwood as tentatively identified in DUL Cosinv.v.17 and NCO MS 1, but being a composite colour, is it difficult to say definitively. In addition, the L*a*b* colour comparisons described earlier in this chapter suggest that each pink is individual (in contrast to the blue colour in each manuscript, which we know to be lapis lazuli and which the L*a*b* results suggest to be homogenous.) Nevertheless, whatever the pink is - Brazilwood or some other organic mixture - it was certainly in ready supply in thirteenth-century France and England, as indicated by its prolific inclusion in all the manuscripts.

Five out of the seven manuscripts have **gold**. It is perhaps slightly unusual that two of the manuscripts of this period do not include it, as it is often a core element in high-grade illumination. It is unlikely that we will ever know the reason for the omission in these cases – a brief lull in supply, an untrained illuminator, or patron preference could all be factors. Interestingly, Cosinv.v.18, one of the manuscripts that does not contain gold (the other being NCO MS 1), is the one that displays **orpiment**. Was this deployed as a substitute for gold?

Apart from the orpiment in Cosinv.v.18, the only other book to contain yellow is NCO MS 20, which features a small quantity of **organic yellow**. The lack of yellow in most of the manuscripts is part of a wider trend - in twelfth-century southern England, for example, orpiment is missing from many manuscripts of the period, attributed to a disruption in supply.[41] This could be because orpiment, the only yellow pigment that is really capable of producing a colour strong enough for illumination, was in short supply at this time – a disrupted trade route from Spain perhaps – and in addition because gold was thought of as superior and the addition of further yellow tones were considered redundant. However, the fact that A.II.3 does not have any yellow on its folios probably adds weight to the evidence suggesting that yellow was not available. One might reasonably expect such lavish illumination to feature all colours obtainable.

Green appears in all seven manuscripts. Considering that malachite is quite abundant in nature, it is perhaps surprising that it is not often seen in manuscripts, and is not identified here, although this is

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[41] Richard Gameson, Andrew Beeby, and Catherine Nicholson, 'Colour at Canterbury', in *Manuscripts in the Making: Art and Science*, vol. 1 (Harvey Miller Publishers, 2018), p.57.

consistent with the wider trend which sees malachite identified only rarely during this time.[42] As malachite is copper-based, it may be that some of the copper greens identified may actually be malachite but that the technology is not yet sensitive enough to allow us to identify it.

Vergaut (a green made from blue and yellow) is identified in one, possibly two of the manuscripts. In A.II.3, the vergaut is a mixture of lapis lazuli and an unknown yellow, the same as the concoction tentatively identified in NCO MS 1. In both manuscripts, an unidentified peak was observed (at 748 cm^{-1} in A.II.3, and 760 cm^{-1} in NCO MS 1). More spectra would be needed to conclude whether or not this peak is emanating from a common source, but it is an intriguing observation. Interestingly, the manuscripts where this mixture of blue and yellow is suspected contain no yellow deployed alone. Again, this is an indicator that the yellow the illuminators possessed was not of sufficient quality to be deployed in its own right. **Copper green**, a catch-all term for several different green pigments, is seen in most of the manuscripts. However, where it is employed, it is only seen in small amounts - it was probably known by the thirteenth century that such green erodes parchment over time and so its use was sparing. In several manuscripts **verdigris,** a common copper green**,** was identified, which is in keeping with what is known about the deployment of green pigments in France in the twelfth and thirteenth century – namely that verdigris was "the pigment of choice".[43]

Whilst commonly employed pigments speak of active trade routes or ease of manufacture, the pigments that are seen infrequently also add to the dialogue. Aside from orpiment, organic yellow, and malachite, already discussed, another pigment rarely seen in this period is **mosaic gold** deployed only in A.II.3.It is a complicated pigment to manufacture, and, as previously mentioned, its use here is an early one. It seems that one of the two artists in that manuscript chose to employ it instead of gold. It was perhaps not known at the time it was employed, given that it was uncommon and novel in the thirteenth century, that its sheen would dull - unlike the gold metal it was replicating. That it is seen in only the most lavish of the seven manuscripts also highlights its rarity.

Another colourstuff rarely seen in thirteenth-century manuscripts, but one that makes an appearance in NCO MS 1, is **folium**. It is widely considered that the thirteenth century is the time when this dye began to be utilised - extracted from turnsole, a plant native to the Mediterranean and the Middle East.[44] Its use in NCO MS 1, therefore, represents an early use of the colourstuff, and

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[42] Paola Ricciardi, Anuradha Pallipurath, and Kristine Rose, '"It's Not Easy Being Green": A Spectroscopic Study of Green Pigments Used in Illuminated Manuscripts', *Analytical Methods* 5, no. 16 (2013), p.3823.

[43] Ricciardi, Pallipurath, and Rose, '"It's Not Easy Being Green"', p. 3820.

[44] P. Nabais et al., 'A 1000-Year-Old Mystery Solved: Unlocking the Molecular Structure for the Medieval Blue from *Chrozophora Tinctoria*, Also Known as Folium', *Science Advances* 6, no. 16 (April 2020), p.3.

links with the fact that NCO MS 1 is of the highest grade. A similar study on a set of high-grade Italian Law books produced in Bologna, northern Italy, in the second half of the thirteenth century, reveals folium was not deployed at that juncture, in Italy.[45]

As well as themes of usage, patterns on the ease of identification also emerge from Table 3. Green - especially copper greens - are hard to characterise specifically, as they absorb the red laser light making Raman identification at the necessary low power challenging. Pinks, discussed previously, are also difficult to ascertain if they are not a mixture of two easily identifiable pigments. Conversely, blues, for example, are fairly straightforward to identify, whether deployed singly or in a mixture.

Further observations also lead to the conclusion that pigment use in the glossed part-Bible is the same as for that for the pocket and larger bibles. This would make sense, as it is a very similar text type produced in the same way, at the same time and with comparable audiences. However, a larger sample of glossed bibles would be needed to state that this was true more generally.

Taken individually, it is clear that one manuscript, DCL A.II.3, stands out as having a wider range of pigments. This is not unexpected - A.II.3 is the largest of the books examined and was made for the lectern. Its high-grade status is echoed in its palette.

Considering the context of the manuscripts also leads to some important observations, chiefly, that there are no discernible differences in the pigments routinely employed in France and in Southern England. Trade routes that supplied France were clearly extending into England during this period. It is perhaps worth remembering that the tidal currents of The Channel meant that crossing the sea from the south coast of England to Northern France was often easier and quicker than sailing between the south and east coasts of England, as can be seen in Figure 85 where, for example, Canterbury and Quentovic are shown as being very easy to navigate between. Having seen in DCL A.IV.30 how styles of artwork were shared and transmitted between the communities in southern England and northern France, it is not a surprise that pigment usage is also comparable. The two areas are closely linked in terms of manuscript production at this time, and that the palette of pigments deployed in both areas is so similar affirms this.

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[45] Richard Gameson et al., 'The Colour of the Law', *Codices Manuscripti et Impressi*, no. 112/113 (2019), p. 1 (Please note that L. Garner is an author on this paper).

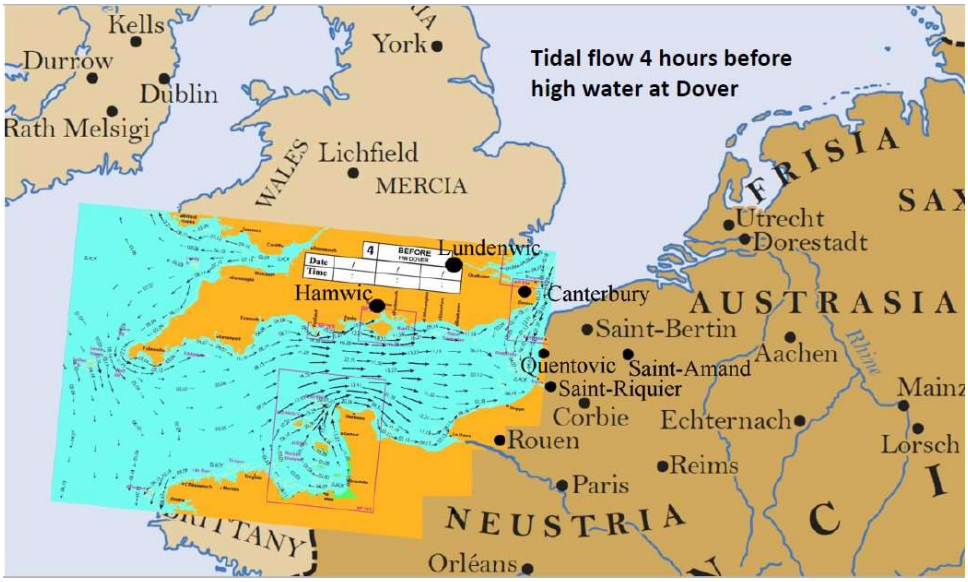

Figure 85: Tidal currents in The Channel in the middle ages.[46]

Discussion of artwork

Repeated use of saturated colours and propensity to deploy plenty of gold is often considered to be 'the paradigm of medieval illumination'.[47] Even a cursory glance at the typical artwork of all seven of the manuscripts reveals this 'paradigm', with striking similarities in the presentation of the artwork contained. An example of a typical initial from each manuscript is collected on page 384 for convenience.[48] In all the manuscripts, an organic dusky pink and a saturated blue dominate the palette. Gold features in most of the manuscripts, utilised in many ways – for the initial itself, for the background to the initial, or to colour part of the scene - as seen in the golden halo and book in DCL A.VI.30 fol. 12r. In DCL A.II.3, gold is used extensively for clothing also – Painter One using gold metal and Painter Two using mosaic gold to achieve a similar effect. White lead is used for faces and hands in all the manuscripts, is sometimes deployed for thin decorative lines, and is utilised often on top of other colours for depicting drapery and contours. Carbon black is similarly used to provide tone and form, and for outlines. Despite the many shades of blue across the seven manuscripts, not once is white lead, or carbon black, seen mixed with lapis lazuli to achieve a lighter or darker blue. Copper

[46] Reproduced by kind permission of Joanna Story, University of Leicester.

[47] Stella Panayotova and Paola Ricciardi, eds., *Manuscripts in the Making: Volume One*, vol. One, Two vols (Harvey Miller, 2017), p. 48.

[48] Whilst DUL Cosinv.v.17 and Cosinv.v.18 do not have any historiated initials, DCL A.IV.37 does, although all the figures depicted are very small, so an additional photomicrograph of a section of the historiated initial is included.

greens and red lead are sparingly deployed, often as vibrant blocks of colour or occasionally modulated with carbon black or white lead.

Figure 86: (left) A close-cropped image of the initial on DCL A.II.3 fol. 100v (Kings), and (right) a typical initial from DUL Cosinv.V.17 fol. 239v.

Figure 87: (left) An initial from DUL Cosinv.V.18 fol. 316 r, (middle) an initial from A.IV.30 fol. 12 r, and (right) the initial on DCL A.IV.37 fol. 337r.

Figure 88: (right) The initial from Job, NCO MS 1 (fol. not recorded), (middle) an initial from NCO MS 20, and (right) a photomicrograph of DCL A.IV.30 fol. 5, showing a figure.

Aside from the black and white shading or lines used to evoke drapery in clothing, pink is often deployed in unadulterated blocks. This is perhaps an indication that the artist was able to pre-mix this colour into the intended shade before application, rather than needing to rely on additional effects added afterwards to obtain the desired result. Alternatively, the pink may be a colourant that was difficult to modify once on the parchment - maybe the pink paint became 'overworked' when additional shading was added – the only colour added to the pink is thin white lines or shading in clothes in A.II.3 and MS. 20 – both the highest-grade manuscripts on which, presumably, the most talented illuminators were working.

Figure 89: NCO MS 20 fol. 1 r mixture of lapis and azurite

The blue in all of the images shown on page 384 is lapis lazuli, occasionally appearing unadulterated, as in DUL Cosin V.v.17 (Figure 86), but more often embellished with white lead decoration or white or black (carbon) shading for the drapery of clothes. That the range of blues shown on page 384 across all the manuscripts is achieved using only lapis lazuli, with white lead, carbon, and occasionally red lead layered on top for shading or decoration, is quite remarkable.

As noted above, it is curious that azurite, which could have been utilised to produce an even wider range of blues, especially in the lavish DCL A.II.3 where it is deployed only for "routine" artwork, is commonly overlooked. In only one manuscript, NCO MS. 20 (which might be considered the second most sumptuous manuscript in this corpus after A.II.3) is azurite mixed with lapis lazuli – seen in Figure 89 above. In Cosinv.v.18, lapis lazuli and azurite are employed in close proximity to provide a range of blue colours but are never actually mixed. Similarly, in NCO MS. 1, azurite is used in a blue initial (see Figure 90) but is deployed in a different area to, and never mixed with, lapis lazuli. For manuscripts that are replete with blue tones, this is perhaps strange. Mixing azurite and lapis lazuli in different quantities would have produced a much wider range of shades of blue than those employed.

Reasons for this sparing use of azurite might be artistic choice or patron preference, but even in this small sample of manuscripts, the restrained use of azurite and the deployment of pure unmixed lapis lazuli appears to be a phenomenon across most hands. The uncommon mixing of blues might have less to do with not wanting to deploy azurite and more to do with not wishing to 'sully' the lapis lazuli – perhaps related to its expense and status – as evidenced above, lapis lazuli was also not seen mixed with carbon or white lead in order to increase its range. Examination of a larger number of thirteenth-century manuscripts would be needed to explore such hypotheses.

Figure 90: The initial on NCO MS 1 fol. 1r.

As mentioned above, DUL A.II.3 and NCO MS 20 stand out as having superior artwork. In A.II.3 there are some very detailed miniature faces (reproduced again in Figure 91) which utilise lapis lazuli, white lead, and vermilion to shade and contour the features. The devil on DCL A.II.3 fol. 2r, seen again in Figure 92**Error! Reference source not found.**, has very many shades of grey created by a mixture of carbon and white lead, with white lead used extensively to detail the face and body. This kind of painterly effect, such as the blending seen on the limbs, is not seen in the other manuscripts which, although skilfully illustrated, are simpler in their artwork and are more reminiscent of the lapis lazuli blue and red lead orange leaves, animals and vines which adorn the devil.

Figure 91: Microscopy images of faces from Paralipomenon on fol. 146 v (left) by Painter One, and (centre and right) from Matthew on fol. 340r by Painter Two.

Figure 92: The Devil, from the General Preface of Jerome, DCL A.II.3 fol. 2r.

Where the artwork in NCO MS 20 reveals itself to be of the highest grade is in its historiated initials. As shown in Figure 93, although the actual figure and animals are simply drawn, the execution of the application of colours and gold is masterful. The colouring of the initial upright using only lapis lazuli, carbon, and white lead is very skilful, as is the application of the gold and its subsequent tooling.

Figure 93: Close-up of the initial of NCO MS 20, fol. 63v.

Figure 94: (left) An image of DUL A.II.3 fol. 2r taken under IR illumination, and (right) the same area under white light.

Although the exact process of the creation of the illuminations may differ from artist to artist and atelier to atelier, in general, designs would be sketched in lead or hardpoint and then inked and painted. As detailed previously in the section on DCL A.II.3 (and shown again in Figure 94), the painter[s] had licence to make a subtle change to the nature of the drawings by painting a longer pen-knife, for example, and felt at liberty to change the drape of the clothing to produce a more pleasing effect.

In all the books examined, carbon was used to delineate painted objects and figures to provide a more polished and neater effect. The carbon outlining was likely added after the painting was complete, and therefore should rather be termed 'overlining'. Infrared images such as those seen above (reproduced here in Figure 95) show the precision of this overlining, which, as an illumination ages, sometimes becomes blurred and not as sharp as it probably once was.

Figure 95: (left) A photomicrograph of the initial on NCO MS.1, and (right) the same initial under infrared illumination.

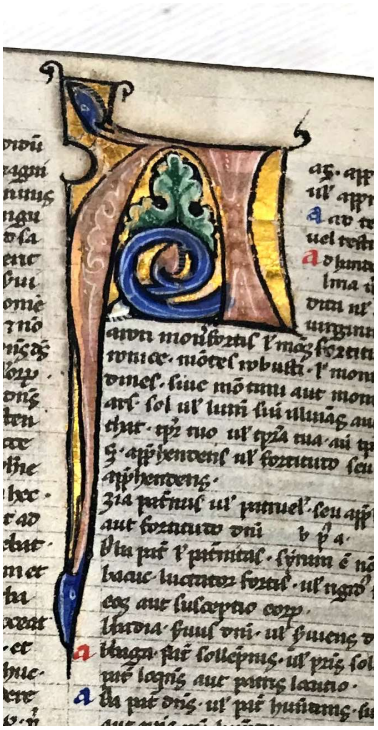

Figure 96: Cosinv.v.17 fol. 292v.

The initial in Figure 96 provides evidence for the process of illumination as described in Chapter Two, and also displays a range of techniques that are deployed across all the manuscripts for the colouration of illuminations. It is clear that in this instance (and in fact, in most instances) the size of the initial is calculated by counting lines – the bowl of the 'P' is exactly eight lines high and the tail extends down a further fifteen lines. Evidently, the lines were drawn before the initial. None of the underdrawings can be seen in this example. Some clues as to the order of the application of paints can be discerned from the fact that the blue curl inside the bowl of the 'p' has accidentally (one

presumes) run over the pink colour, which must have been laid down previously. Similarly, the fact that the gold encroaches on top of the pink and green areas hints that this was one of the last colourants to be applied. The black contour lines sometimes run over the gold, other times under it - this suggests that the black outlining was painted before the gold was applied, and the passage of time has allowed the gold to creep over the black lines.

The initial in Figure 96 also showcases an example of white lead being used to decorate and embellish colours – as seen on the blue and pink. White lead is also employed here to lighten a pigment, as seems to be the case in the green foliate decoration at the top. Three zones of green can be seen - dark in the centre at the bottom, a lighter green surrounding it, and a pale light green around that – with a very thin white line outlining the whole form. It would seem that this effect has been produced with the addition of varying amounts of white lead to a green paint already laid down, rather than three green paints having been mixed and applied. Again, this is consistent with what has been found in all of the manuscripts examined: that mixtures are rare, and shades and tones of colours are usually created by the later application of (lead) white or black (carbon).

Figure 97: (right) The initial from Job, NCO MS 1 (fol. not recorded), (middle) an initial from NCO MS 20, and (right) a photomicrograph of DCL A.IV.30 fol. 5 showing a figure.

As mentioned, this rarity of mixtures and zonal overpainting of carbon or white lead where necessary is particularly seen in the clothing in all the manuscripts. As shown in all the initials on page 384 (reproduced in Figure 97 for ease) the draped effect in the clothing is realised by over painting and shading on top of a block of colour applied, rather than by applied several different pre-mixed paints. In the initial from Job blue can be seen overpainted with black to produce the desired drapery effect – there is no mixing or blending. Whilst less "painterly" than other painting styles, this pragmatic approach would seem to be the most obvious choice for a painter in a busy atelier, where time and economic considerations would, no doubt, have been a factor.

Change of hands in artwork

As mentioned above, A.II.3 has at least two hands painting the illuminations, as betrayed by the choice of gold or mosaic gold, and by slightly different styles of rendering the background. However, the faces of the figures in each artist's section are very similar, as seen in Figure 98, where, despite horns and facial hair, the two faces are painted in a very similar style. The style of the faces could be attributed to the painters having been schooled in a particular way of generating the faces, or could be attributed to the artist producing sufficiently styled underdrawings that any overpainting artist could adhere to.

Figure 98: (left) DCL A.II.3 fol. 20 r, and (right) fol. 358r.

In DUL Cosinv.v.18, DCL A.IV.30 and DCL A.IV.37 there is insufficient artwork to allow noticeable differences between hands, if indeed there are different hands, to come to light. In NCO MS 1 and MS 20, there were no discernible differences in hands throughout the book.Cosinv.v.17 does perhaps have more than one painter, as some of the initials use a vibrant pink that is not found in the rest of the artwork, and the initials that feature this colour are, on the whole, simpler in conception than the others, an example of which is seen in Figure 99. However, without more robust evidence, this is speculation.

Figure 99:The initial from DUL Cosinv.v.17 fol. 239v.

Broader Context

Very little reliable scholarship has been published on the pigments of thirteenth-century French and English manuscripts – making this thesis so relevant. However, as mentioned in chapter one, *The Art and Science of Illuminated Manuscripts: A Handbook* was published in 2021 (hereafter referred to as *'The Handbook'*)[49] , and ten of its fifty-eight case studies are relevant to the present work in that they concern volumes made in Northern France or Southern England during the thirteenth century.

This little corpus comprises three psalters, a psalter-hours, two apocalypses, two bibles, a pontifical, and a copy of *La Somme le Roi*. Dating from 1210 to 1316, six are from Northern France (four specifically from Paris) and four were made in England. Table 4 below details the colourants identified in these manuscripts.

Like the seven manuscripts investigated in this thesis, pink and blue characterise the palette in many of the selected handbook items. In addition, clear 'staple' pigments are found in the handbook manuscripts (vermilion, carbon, white lead, red lead, organic pink and copper green), echoing the findings of the works in this thesis. Taking these ten books along with the seven analysed in this study provides a reasonable sample for ascertaining the typical palette of the thirteenth century in these regions. Certainly, enough data is provided to allow glaringly incongruous occurrences to be spotted, e.g. the lack of vermilion in SJCC MS K.26 Psalter cuttings, which cannot really be attributed to anything other than circumstance or artist preference.

The absence of lapis lazuli from two of the volumes produced earlier in the century (Fitz' MS 2-2011 and the William de Brailes Psalter) is unusual, particularly at a time when lapis lazuli seems to be in plentiful supply and dominates the palette in all the other manuscripts. There is certainly an intriguing pattern with the deployment of azurite and indigo. Indigo does not appear in any manuscripts examined until mid-century when it appears in boles and then later in the artwork proper. Azurite's deployment is patchy throughout the century, both in the handbook manuscripts and the manuscripts examined in this study. It could seem as if indigo and azurite are deployed as alternatives to each other – where azurite is seen, indigo is not - and vice versa. This might not be that unusual - in addition to lapis lazuli, two other blues may have been one blue too many! However, the apparent preference for using only one of indigo or azurite appears to diminish towards the end of the century when it seems both were deployed, in addition to lapis lazuli. There

[49] Stella Panayotova, ed., *The Art & Science of illuminated manuscripts: A handbook.* (New York: Brepols N.V., 2020).

is certainly not enough data in these seventeen manuscripts to define the pattern here, but this collection is a good starting point for further research.

Gold is found in all of the handbook manuscripts, highlighting the absence of gold in DUL Cosinv.v.18 and NCO MS 1 as more unusual. It is clear from the work done on the differing colours of bole in the handbook that the thirteenth century was a time for exploration of how to produce changing tones within the leaf - with different coloured boles producing different effects.

The deployment of a purple dye in the very early fourteenth-century manuscript Fitzwilliam Museum MS 298, and only then by a pioneering artist, confirms the occurrence of purple in NCO MS. 1 up to fifty years earlier as particularly noteworthy. Similarly, the absence of mosaic gold in any of the manuscripts studied in *The Handbook* exposes its deployment in DCL A.II.3 as even more singular.

Another pigment that was identified rarely in *The Handbook* manuscripts was lapis ash. However, this may be due to differences in descriptive terminology between the two teams that examined the different volumes. What Team Pigment refer to as lapis ash may be described as low-grade ultramarine by MINIARE. Similar differences occur in the identification of verdigris/copper green and organic red/pink between the two groups.

Considering the seventeen manuscripts as a whole, a staple thirteenth-century palette emerges, as detailed above. Furthermore, the deployment of colourants leads to the conclusion that there is no discernible difference in the palette of northern French illuminators and their contemporaries in southern England. Indeed, the grade and importance of the book at the time of manufacture have more bearing on the range and choice of colourants deployed.

	A Selection of pertinent manuscripts examined in *The Art and Science of Illuminated Manuscripts: A Handbook*									
	Fitz' Museum - MS 2-2011	Fitz Museum MS McClean 11 (	Fitz' Museum and Morgan Lib & Museum - W. de Brailes Psalter	Fitz' Marlay Cuttings Fr. 1A.1, 1A.2, 1A.3, 1A.4, 1A.5, and 1A.6)	TCC MSr.16.2	Fitz MS 300 and MS lat. 10525	LPL MS 209 The Lambeth Apocalypse England, prob	SJCC MS K.26 Psalter cuttings	MSS 192 and 368 leaves from Laurent d' Orléans	Fitz' Museum MS 298Pontifical of Renaud de Bar
Vermilion	✓	✓	✓	✓	✓	✓	✓		✓	✓
Red lead	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Brazilwood										
Organic Pink	✓*	✓*		✓*	✓*	*	✓*	✓*		✓*
Organic Yellow		✓	✓	✓		✓*		✓		✓*
Orpiment			✓*		✓			✓		✓
Malachite										
Copper Green			✓							
Verdigris	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Vergaut								✓*		✓*
Lapis Lazuli		✓		✓	✓	✓	✓	✓	✓	✓
Azurite	✓		✓	*	✓			✓	?✓	✓
Indigo				✓	✓	✓	✓	✓*	✓	✓
Organic Purple										✓

	Folium										
	White lead	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	Gypsum			✓	✓*	✓	✓	✓	✓	✓	✓
	Lapis ash				✓*						
	Carbon		✓	✓	✓	✓	✓	✓	✓	✓	✓
	Gold	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	Mosaic Gold										

Table 4: A chart showing pigments and dyes identified in The Handbook.

Notes: For many of the manuscripts in the table, whereas the authors refer to "Organic red", I refer in the table to "Organic Pink".

***Fitzwilliam Museum MS 2-2011** - the organic pink is plant-derived.*

***MS McClean 11** - the organic red is identified as insect-based.*

***William de Brailes Psalter Miniatures** also contains many different colour earths, and possible lead oxide in the yellow colourant. Silver leaf also found.*

***The Marlay cuttings** contain either a mixture of chalk/gypsum or a low-grade lapis lazuli (lapis ash). This is my own supposition from the information provided by the authors. Azurite is found in later retouches only.*

***Trinity Apocalypse** possibly has chalk instead of gypsum as well as yellow, red and brown earths, shell silver and silver leaf in addition to the pigments listed. Yellow is arsenic-based but not confirmed as orpiment. The organic pink is insect-derived.*

***Psalter hours - MS 300** contains gypsum and chalk that is not yet identified in MS Lat. 10525; aside from that, the colourants identified are identical. The organic red is insect-derived. Organic yellow tentatively identified.*

***The Lambeth Apocalypse** also contains yellow and brown earth, iron gall ink, organic red insect-derived, with silver leaf present.*

***MS K.26 Psalter cuttings** - the indigo was possibly deployed only as part of a vergaut. Green and red earths, and shell silver was applied as a later addition. Orpiment and chalk are tentative identifications. organic red insect-derived*

***Leaves from Laurent d'Orléans** contain brown earth, shell gold and shell silver in addition.*

***Pontifical** iron gall ink, red earth later additions only, insect-derived organic pink, organic yellow could be lead oxide, e.g. massicot, shell silver later additions.*

Conclusion

Primarily, this thesis is 'novel' because the manuscripts it includes have never before been examined scientifically, and thus all the data and subsequent analysis that is contained is 'new'. However, to churn out data from a hitherto unexamined manuscript is not sufficient - as Ricciardi states in her editorial to *Heritage Science,* the field of scientific examination of manuscripts has "moved past the naïve enthusiasm that used to follow every identification of an (often very common) pigment on a manuscript page".[1] Therefore, this thesis crucially also considers the context for, and potential meaning behind, the choice of pigments on the page. Furthermore, this study takes the seven manuscripts as a corpus and later compares them to ten other similar thirteenth-century books, meaning that patterns and trends that emerge from a representative sample of manuscripts in a particular time and place can be identified.

In summary, the palette of the seven manuscripts examined here is broadly in keeping with what might be expected of manuscripts in the thirteenth century in Northern France and Southern England. Several 'workhorse' pigments that one might assume for a high-grade manuscript of the time, outlined in Chapter Two, are present – lapis lazuli, vermilion, red lead, white lead, copper green, and carbon - in the quantities anticipated. However, there are a few noteworthy anomalies to the expected palette that are again highlighted here, as they are evidence that may now be used to form part of the wider picture of pigment use in the thirteenth century.

The deployment of mosaic gold in DCL A.II.3, a manuscript whose creation date is dated to c.1260, is an unusually early example of this pigment.[2] As mentioned in *Colour: The Art and Science of Illuminated manuscripts,* mosaic gold has yet to be identified in any manuscript before the second half of the century.[3]

Folium was found in NCO MS 1. Its deployment in a manuscript of this time is striking, as, despite having been seen in the sixth-century manuscript The Sinope Gospels (also known as the Codex Sinopensis Paris, Bibliothèque Nationale, MS gr. 1286) , it is rarely identified in European manuscripts.[4]

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[1] Paola Ricciardi, 'Manuscripts in the Making: Art and Science', *Heritage Science* 7, no. 1 (2019), p.1.
[2] 'Durham Durham Cathedral MS A.II.3 - Durham Priory', accessed 18 February 2021, https://www.durhampriory.ac.uk/mediawiki/Durham_Durham_Cathedral_MS_A.II.3.
[3] Stella Panayotova et al., eds., *Colour: The Art & Science of Illuminated Manuscripts* (London Turnhout: Harvey Miller Publishers, 2016), p. 198.
[4] Mark Clarke, *Mediaeval Painters' Materials and Techniques: The Montpellier Liber Diversarum Arcium* (London: Archetype, 2011),p. 120.

As discussed, identification of purple in manuscripts can be problematic, so this tentative identification by mathematical methods applied to a FORS spectrum may simply be a symptom of the difficult nature of purple colourants, or it may be a noteworthy rare deployment of folium. As technology improves and more thirteenth-century manuscripts are analysed, this issue may be resolved.

That very little yellow colouration is seen across all the manuscripts fits in with a wider trend but is still worthy of note, as is the absence of gold in two of the manuscripts.

Regarding blue pigments, that lapis lazuli is found in every manuscript is not unexpected, but there is a pattern of more restrained use of the pigment when compared to the almost profligate deployment of the pigment in the twelfth century, when large full-page miniatures in the substances are seen in books, as well as the copious amounts in wall paintings, at Canterbury Cathedral, for example.[5] The scarcity of indigo deployed in the books and the erratic deployment of azurite is also remarkable.

That Brasilwood is tentatively identified in DUL Cosin V.v.17 and in NCO MS1 is striking, as this pigment is not commonly reported.

The deployment of lapis lazuli in all manuscripts was confirmed by Raman spectroscopy and FORS but was also found to be similar in all manuscripts when examined in L*a*b* colourspace. Conversely, when examined in the same way, the pink colour was found to be different in most of the manuscripts, suggesting its components and/or methods of preparation differ. This method of comparison of colourants in manuscripts, whilst not diagnostic and rudimentary at present, is, to my knowledge, original and is one that could be developed to become a method of colour comparison between manuscripts with further testing on different data sets.

This thesis sits comfortably in the corpus of work that Team Pigment has undertaken and is comparable to that published to date in terms of rigour, technique, and subject matter. As seen in Chapter One, Team Pigment's work varies from the scientific and art-historical analysis of medieval manuscripts on a small scale - *The Admiral, the Virgin, and the Spectrometer: Observations on the Coëtivy Hours (Dublin, Chester Beatty Library, MS W082*), for example, to the large scale - the diachronistic study of Canterbury made books from the tenth to the twelfth century and the even larger forthcoming AHRC project on pigments in The British Isles from the fifth to the fifteenth century.

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[5] Helen Howard, *Pigments of English Medieval Wall Painting* (London: Archetype, 2003), p. 28-29; Richard Gameson et al., 'Late Medieval English Illuminators' Blues', (forthcoming).

[6] This work could be seen as a companion work to *The Colour of the Law*, an analysis by Team Pigment of the pigments and artwork in a small group of fourteenth-century Italian Law books, published in *Codices Manuscripti et Impressi* in 2019.[7]

Technologically, the examination undertaken on all manuscripts exemplifies the rules of good practice surrounding safe and non-invasive manuscript examination as mentioned in *There is more to spectroscopy than lux*, ensuring that no manuscript receives damaging levels of laser energy.[8] Techniques that are routinely employed by Team Pigment – Raman spectroscopy, FORS in the UV-Vis-NIR-SWIR range, and multispectral imaging have similarly been applied in this thesis.

Similar works from other research groups are the Panayotova et al. study on fourteenth-century manuscript artworks, further indicating the legitimacy of such tightly focused studies as part of a wider effort to gain an understanding of trends in pigment usage.[9] As is clear from the wider body of scholarship presented in Chapter One, there has been little work on thirteenth-century Parisian pigments and pigments in Paris Bibles more generally, and thus this work is a remedy to that lacuna. It is another piece in the jigsaw of pigment use in time and place.

On the work of pigment identification, this work also agrees with the hypothesis put forward by Aceto that the colour of folium is not pH-dependent, as is widely stated in scholarship, and agrees with the identification of folium by its 1/logR double inflection point.[10] Thus, this thesis disagrees with the recent findings by the University of Lisbon that state that folium cannot be identified in this way and has a different reflectance spectrum.[11] Clearly, this is an area where there are different viewpoints and one that is currently being researched, so further developments in this area, and in the arena of identification of purple colourants more generally, are expected to emerge, and this thesis should then be reviewed in that light.

---

[6] Richard Gameson, Catherine Nicholson, and Andrew Beeby, 'The Admiral, the Virgin, and the Spectrometer: Observations on the Coëtivy Hours (Dublin, Chester Beatty Library, MS W082)', *Gesta*, 14 October 2020.
[7] Richard Gameson et al., 'The Colour of the Law', *Codices Manuscripti et Impressi*, no. 112/113 (2019).
[8] Andrew Beeby et al., 'There's More to Reflectance Spectroscopy than Lux', *Journal of the Institute of Conservation*, 8 May 2018, 1–12. Please note L. Garner is an author on this paper.
[9] Stella Panayotova, Paola Ricciardi, and Lucía Pereira-Pardo, 'Illuminators' Materials and Techniques in Fourteenth-Century English Manuscripts', in *Manuscripts in the Making*, ed. Stella Panayotova and Paola Ricciardi, vol. 1, 2 vols (Harvey Miller, 2017), 46–63.
[10] Maurizio Aceto et al., 'Characterisation of Colourants on Illuminated Manuscripts by Portable Fibre Optic UV-Visible-NIR Reflectance Spectrophotometry', *Analytical Methods* 6, no. 5 (2014), p.1491; Maurizio Aceto et al., 'On the Identification of Folium and Orchil on Illuminated Manuscripts' 171 (January 2017), p. 463.
[11] P. Nabais et al., 'A 1000-Year-Old Mystery Solved: Unlocking the Molecular Structure for the Medieval Blue from *Chrozophora Tinctoria*, Also Known as Folium', *Science Advances* 6, no. 16 (April 2020).

Future work

It is clear that there is scope for a wider scale study of pigments in Paris Bibles, and this could be tackled in numerous ways. Most prosaically, this wider study could be a random sample of bibles in the Paris Bible genre selected by current location and ease of access. These are not arbitrary considerations when one remembers that all personnel and equipment must be transported to the site of the manuscript and that analysis undertaken must avail of the host intuition no small amount of help and hospitality. However, if these considerations are mitigated, then more Paris Bibles could be examined, grouped by size, location of creation, or by atelier – even by illuminating artist if that much is known.

Leaving aside the ecclesiastic text type, investigation into pigments and dyes employed before, during and after the thirteenth century in Paris could be investigated, with any manuscript containing colours analysed. This could produce a study similar to *Colour at Canterbury* – affording a diachronistic study of pigments in one place.[12]

On a wider scale, this study could feed into data that could produce a handbook similar to that currently underway by Team Pigment, where colourants from the fifth to the fifteenth century in the British Isles are examined. Pigments and dyes deployed within France, or indeed across Northern or Western Europe, over an extended time period, could be examined.

Further questions raised by this thesis concern deployment (and to some extent secure identification) of purple colourants in the thirteenth century - alongside detection and deployment of the ubiquitous organic pink. These inquiries might be addressed by the investigations proposed above, and certainly, a more encompassing study would provide further details on the intriguing deployment of blue pigments that this study has begun to unearth.

By combining the data obtained by utilising the latest technological and scientific equipment with the most pertinent scholarship, this thesis has gone some way towards remedying the lacuna in pigment and dye analysis of the artwork in thirteenth-century northern European manuscripts. With the expected palette now securely defined by this thesis, the stage is set for further research and examination of thirteenth-century manuscripts.

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[12] Richard Gameson, Andrew Beeby, and Catherine Nicholson, 'Colour at Canterbury', in *Manuscripts in the Making: Art and Science*, vol. 1 (Harvey Miller Publishers, 2018).

Appendices

A - MatLab code to produce a false colour image (as described in Chapter Three)

B - MatLab code to loop through a folder and plot FORS spectra and its Kubelka-Munk transformation (as described in Chapter Three)

C - MatLab code to change the test function (testfunc) to improve labelling on FORS spectra

D - MatLab code to loop through a folder and plot Raman spectra with background correction (backcor) as detailed in Chapter Three

E - MatLab code to change the test function (testfunc) to improve labelling on Raman spectra

F - MatLab code to perform Background correction "Backcor" on Raman spectra with a GUI, as detailed in Chapter Three

G - MatLab code to produce a scatter plot of (e.g. pink) L*a*b* pixels from an RGB single colour image, as described in Chapter Three

Appendix A
MatLab code to produce a false colour image

This code was written by Prof. A. Beeby of Durham University.

```
% import blue, green read and IR images as f2, f4, f6 and f9 respectively

% register NIR image correctly by shifting 15, 0 pixels

f9t=imtranslate(f9,[15,0]);


%create rgb image with approx balanced colours

pic(:,:,1)= f6(:,:,1)*1.05;

pic(:,:,2)= f4(:,:,1)*0.8;

pic(:,:,3)= f2(:,:,1);


%create false colour image

fpic(:,:,1)= f9t(:,:,1)*0.8;

fpic(:,:,2)= f6(:,:,1);
```

```
fpic(:,:,3)= f2(:,:,1);

%now plot
figure(1)
imshow(pic);
figure(2)
imshow(fpic);

figure(3)
subplot(2,1,1);
imshow(pic);
subplot(2,1,2);
imshow(fpic);
```

Appendix B

MatLab code to loop through a folder and plot FORS spectra and its Kubelka-Munk transformation

```
This code was written by Louise Garner, assisted by Andrei Markin, Durham University
clear
%[file,path,indx] = uigetfile('*.txt');
% if isequal(file,0)
%    %disp('User selected Cancel')
% else
%    %disp(['User selected ', fullfile(path, file),...
%    %      ' and filter index: ', num2str(indx)])
%    f =  fullfile(path,file);
%
txtfiles = dir('*.txt') ;
```

```
N = length(txtfiles) ;
for i = 1:N
thisfile = txtfiles(i).name ;

data = dlmread(thisfile);
xd = data(:,1);
yd = data(:,2);

x = [xd(1:1131); xd(1663:end)];
y = [yd(1:1131); yd(1663:end)];
%---------------------------
figure
y = smooth(y,10);
plot(x,y);
%y = smooth(y);

ax = gca;
ax.FontSize = 18;
xlabel('Wavelength \ nm','fontsize',20);
ylabel('Refelction','fontsize',20);
%ylim([0 inf])
xlim([450 inf])
%figure
box off

newname = [thisfile, '_raw'];
filename = [newname,'.fig'];
saveas(gcf, filename);
filename = [newname,'.jpg'];
```

```
saveas(gcf, filename);

figure
%y=y./100;
% y1=power(1-y,2)./(2.*y);
% %y1=smooth(y1);
% plot(x,y1);

figure;
y2=(1/y);
y3=log(y2);
plot(x,y3);

ax = gca;
ax.FontSize = 18;
xlabel('Wavelength \ nm','fontsize',20);
ylabel('Refelction','fontsize',20);
ylim([0 inf])
xlim([0 inf])
figure
box off

newname = [thisfile, '_KM'];
filename = [newname,'.fig'];
saveas(gcf, filename);
filename = [newname,'.jpg'];
saveas(gcf, filename);
  %----------------------
End
```

Appendix C

MatLab code to change the test function (testfunc) to improve labelling on FORS spectra

This code was written by Louise Garner

```
function output_txt = myfunction(obj,event_obj)
% Display the position of the data cursor
% obj          Currently not used (empty)
% event_obj    Handle to event object
% output_txt   Data cursor text string (string or cell array of strings).

pos = get(event_obj,'Position');
output_txt = {[' ',num2str(pos(1),4),'']};

alldatacursors = findall(gcf,'type','hggroup')
set(alldatacursors,'FontSize',20)
set(alldatacursors,'FontName','Calibri')
set(alldatacursors, 'FontWeight', 'normal')
set(alldatacursors, 'BackgroundAlpha', 0)
set(alldatacursors, 'EdgeColor', [1 1 1])
set(alldatacursors, 'MarkerEdgeColor', [1 1 1])
%set(alldatacursors, 'Interpreter','latex')

% If there is a Z-coordinate in the position, display it as well
if length(pos) > 2
   output_txt{end+1} = ['Z: ',num2str(pos(3),4)];
end
```

Appendix D

MatLab code to loop through a folder and plot Raman spectra with background correction (backcor)

This code was written by Louise Garner, assisted by Andrei Markin, Durham University

```
%list folder files
files = dir('*.asc');

for k=1:length(files)
  %get file name
  fname = files(k).name;
  %run your code on the current file
  myFunction(fname,k);
end

function myFunction(fname,k)
  %%your code....
  T=dlmread(fname);
x=T(:,1);
y=T(:,end);

figure;
plot(x,y)
%ylim([0 inf])
ax = gca;
ax.FontSize = 18;
xlabel('Raman Shift / cm^{-1}','fontsize',20);
ylabel('Intensity','fontsize',20);
```

```
box off
%ylim([0 inf])

newname = [fname, '_raw'];
filename = [newname,'.fig'];
saveas(gcf, filename);
newname = [fname, '_raw'];
filename = [newname, '.jpg'];
saveas(gcf, filename);

figure;
n=backcor(x,y);
y=y-n;
plot (x,y);
ax = gca;
ax.FontSize = 18;
xlabel('Raman Shift / cm^{-1}','fontsize',20);
ylabel('Corrected Intensity','fontsize',20);
ylim([0 inf])
box off

newname = [fname, '_backcor'];
filename = [newname,'.fig'];
saveas(gcf, filename);

figure;
y = smooth(y,20);
plot(x,y)
xlabel('Raman Shift / cm^{-1}','fontsize',20);
```

```
ylabel('Corrected intensity','fontsize',20);
ax = gca;
ax.FontSize = 18;
ylim([0 inf])
box off

newname = [fname, '_backcorsmooth'];
filename = [newname,'.fig'];
saveas(gcf, filename);
end
```

Appendix E

MatLab code to change the test function (testfunc) to improve labelling on Raman spectra

This code was written by Louise Garner

```
function output_txt = myfunction(obj,event_obj)
% Display the position of the data cursor
% obj          Currently not used (empty)
% event_obj    Handle to event object
% output_txt   Data cursor text string (string or cell array of strings).

pos = get(event_obj,'Position');
output_txt = {[' ',num2str(pos(1),4),'']};

alldatacursors = findall(gcf,'type','hggroup')
set(alldatacursors,'FontSize',20)
set(alldatacursors,'FontName','Calibri')
```

```
set(alldatacursors, 'FontWeight', 'normal')
set(alldatacursors, 'BackgroundAlpha', 0)
set(alldatacursors, 'EdgeColor', [1 1 1])
set(alldatacursors, 'MarkerEdgeColor', [1 1 1])
%set(alldatacursors, 'Interpreter','latex')

% If there is a Z-coordinate in the position, display it as well
if length(pos) > 2
   output_txt{end+1} = ['Z: ',num2str(pos(3),4)];
end
```

Appendix F

MatLab code to perform Background correction "Backcor" on Raman spectra with a GUI, as detailed in Chapter Three

For further information on authorship please see:

V. Mazet, C. Carteret, D. Brie, J. Idier, B. Humbert. Chemom. Intell. Lab. Syst. 76 (2), 2005

```
function [z,a,it,ord,s,fct] = backcor(n,y,ord,s,fct)
% BACKCOR   Background estimation by minimizing a non-quadratic cost function.
%   [EST,COEFS,IT] = BACKCOR(N,Y,ORDER,THRESHOLD,FUNCTION) computes and estimation EST
%   of the background (aka. baseline) in a spectroscopic signal Y with wavelength N.
%   The background is estimated by a polynomial with order ORDER using a cost-function
%   FUNCTION with parameter THRESHOLD. FUNCTION can have the four following values:
%      'sh'  - symmetric Huber function :  f(x) = { x^2  if abs(x) < THRESHOLD,
%                                                 { 2*THRESHOLD*abs(x)-THRESHOLD^2  otherwise.
%      'ah'  - asymmetric Huber function :  f(x) = { x^2  if x < THRESHOLD,
%                                                  { 2*THRESHOLD*x-THRESHOLD^2  otherwise.
%      'stq' - symmetric truncated quadratic :  f(x) = { x^2  if abs(x) < THRESHOLD,
```

```
%                                       { THRESHOLD^2  otherwise.
%     'atq' - asymmetric truncated quadratic :  f(x) = { x^2  if x < THRESHOLD,
%                                       { THRESHOLD^2  otherwise.
%   COEFS returns the ORDER+1 vector of the estimated polynomial coefficients
%   (computed with n sorted and bounded in [-1,1] and y bounded in [0,1]).
%   IT returns the number of iterations.
%   [EST,COEFS,IT] = BACKCOR(N,Y) does the same, but run a graphical user interface
%   to help setting ORDER, THRESHOLD and FCT.
% For more informations, see:
% - V. Mazet, C. Carteret, D. Brie, J. Idier, B. Humbert. Chemom. Intell. Lab. Syst. 76 (2), 2005.
% - V. Mazet, D. Brie, J. Idier. Proceedings of EUSIPCO, pp. 305-308, 2004.
% - V. Mazet. PhD Thesis, University Henri Poincaré Nancy 1, 2005.
%
% 22-June-2004, Revised 19-June-2006, Revised 30-April-2010,
% Revised 12-November-2012 (thanks E.H.M. Ferreira!)
% Comments and questions to: vincent.mazet@unistra.fr.
% Check arguments
if nargin < 2, error('backcor:NotEnoughInputArguments','Not enough input arguments'); end;
if nargin < 5, [z,a,it,ord,s,fct] = backcorgui(n,y); return; end; % delete this line if you do not need GUI
if ~isequal(fct,'sh') && ~isequal(fct,'ah') && ~isequal(fct,'stq') && ~isequal(fct,'atq'),
   error('backcor:UnknownFunction','Unknown function.');
end;
% Rescaling
N = length(n);
[n,i] = sort(n);
y = y(i);
maxy = max(y);
dely = (maxy-min(y))/2;
n = 2 * (n(:)-n(N)) / (n(N)-n(1)) + 1;
```

```
y = (y(:)-maxy)/dely + 1;
% Vandermonde matrix
p = 0:ord;
T = repmat(n,1,ord+1) .^ repmat(p,N,1);
Tinv = pinv(T'*T) * T';

% Initialisation (least-squares estimation)
a = Tinv*y;
z = T*a;
% Other variables
alpha = 0.99 * 1/2;     % Scale parameter alpha
it = 0;                 % Iteration number
zp = ones(N,1);         % Previous estimation

% LEGEND
while sum((z-zp).^2)/sum(zp.^2) > 1e-9,
   it = it + 1;         % Iteration number
   zp = z;              % Previous estimation
   res = y - z;         % Residual

   % Estimate d
   if isequal(fct,'sh'),
      d = (res*(2*alpha-1)) .* (abs(res)<s) + (-alpha*2*s-res) .* (res<=-s) + (alpha*2*s-res) .* (res>=s);
   elseif isequal(fct,'ah'),
      d = (res*(2*alpha-1)) .* (res<s) + (alpha*2*s-res) .* (res>=s);
   elseif isequal(fct,'stq'),
      d = (res*(2*alpha-1)) .* (abs(res)<s) - res .* (abs(res)>=s);
   elseif isequal(fct,'atq'),
      d = (res*(2*alpha-1)) .* (res<s) - res .* (res>=s);
```

```
    end;

    % Estimate z
    a = Tinv * (y+d);   % Polynomial coefficients a
    z = T*a;            % Polynomial

end;

% Rescaling
[~,j] = sort(i);
z = (z(j)-1)*dely + maxy;

    a(1) = a(1)-1;
    a = a*dely;% + maxy;
end
% delete lines below if you do not need GUI
function [z,a,it,ord,s,fct] = backcorgui(n,y)
% BACKCORGUI   Graphical User Interface for background estimation.
% Initialization
z = [];
a = [];
it = [];
ord = [];
s = [];
fct = [];
order = 7;
threshold = 0.01;
costfunction = 'atq';
% Main window
```

```
hwin = figure('Visible','off','Position',[0 0 750 400],'NumberTitle','off','Name','Background Correction',...
   'MenuBar','none','Toolbar','figure','Resize','on','ResizeFcn',{@WinResizeFcn});
bgclr = get(hwin,'Color');

% Axes
haxes = axes('Units','pixels');

% Buttons OK & Cancel
hok =
uicontrol('Style','pushbutton','String','OK','Position',[600,40,80,25],'Callback',{@OKFcn},'BackgroundColo
r',bgclr);
hcancel =
uicontrol('Style','pushbutton','String','Cancel','Position',[510,40,80,25],'Callback',{@CancelFcn},'Backgro
undColor',bgclr);

% Cost functions menu
hfctlbl = uicontrol('Style','text','String','Cost
function:','HorizontalAlignment','left','BackgroundColor',bgclr);
hfct =
uicontrol('Style','popupmenu','Value',4,'BackgroundColor','white','Callback',{@CostFunctionFcn},...
   'String',{'Symmetric Huber function','Asymmetric Huber function','Symmetric truncated
quadratic','Asymmetric truncated quadratic'});

% Threshold text
hthresholdlbl =
uicontrol('Style','text','String','Threshold:','HorizontalAlignment','left','BackgroundColor',bgclr);
hthreshold =
uicontrol('Style','edit','String',num2str(threshold),'BackgroundColor','white','Callback',{@ThresholdFcn});

% Order slider
horderlbl = uicontrol('Style','text','String','Polynomial
order:','HorizontalAlignment','left','BackgroundColor',bgclr);
```

```
horder = uicontrol('Style','slider','SliderStep',[0.5 0.5],'Min',0,'Max',10,'Value',order,'SliderStep',[0.1
0.1],'Callback',{@OrderFcn});

horderval = uicontrol('Style','text','String',num2str(order),'BackgroundColor',bgclr);


% Move the GUI to the center of the screen

movegui(hwin,'center');


% Plot a first estimation

[ztmp,atmp,ittmp,order,threshold,costfunction] = compute(n,y,order,threshold,costfunction);


% Make the GUI visible

set(hwin,'Visible','on');


% Callback functions


   function CancelFcn(source,eventdata)

      % Just close the window

      uiresume(gcbf);

      close(hwin);

   end


   function OKFcn(source,eventdata)

      % Return the current estimation and close the window

      z = ztmp;

      a = atmp;

      it = ittmp;

      ord = order;

      s = threshold;

      fct = costfunction;
```

```
    uiresume(gcbf);
    close(hwin);
end

function CostFunctionFcn(source,eventdata)
    % Change cost function
    cf = get(hfct,'Value');
    if cf == 1,
        costfunction = 'sh';
    elseif cf == 2,
        costfunction = 'ah';
    elseif cf == 3,
        costfunction = 'stq';
    elseif cf == 4,
        costfunction = 'atq';
    end
    [ztmp,atmp,ittmp,ord,s,fct] = compute(n,y,order,threshold,costfunction);
end

function OrderFcn(source,eventdata)
    % Change order
    order = get(horder,'Value');
    set(horderval,'String',num2str(order));
    [ztmp,atmp,ittmp,ord,s,fct] = compute(n,y,order,threshold,costfunction);
end

function ThresholdFcn(source,eventdata)
    % Change threshold
    threshold = get(hthreshold,'String');
```

```
   threshold = str2double(threshold);
   [ztmp,atmp,ittmp,ord,s,fct] = compute(n,y,order,threshold,costfunction);
end

function [ztmp,atmp,ittmp,order,threshold,costfunction] = compute(n,y,order,threshold,costfunction)
   % Compute and plot an estimation (need to sort the data)
   [ztmp,atmp,ittmp,order,threshold,costfunction] = backcor(n,y,order,threshold,costfunction);
   [~,i] = sort(n);
   plot(n(i),y(i),'b-',n(i),ztmp(i),'r-');
end

function WinResizeFcn(source,eventdata)
   % Resize the window
   pos = get(hwin,'Position');
   w = pos(3);
   h = pos(4);
   if w>400 && h>100,
      set(haxes,'Position',[40,40,w-320,h-70]);
   end;
   set(hok,'Position',[w-90,30,80,25]);
   set(hcancel,'Position',[w-180,30,80,25]);
   set(hfctlbl,'Position',[w-240,h-30,220,20]);
   set(hfct,'Position',[w-240,h-50,220,25]);
   set(hthresholdlbl,'Position',[w-240,h-80,220,20]);
   set(hthreshold,'Position',[w-240,h-100,220,20]);
   set(horderlbl,'Position',[w-240,h-130,220,20]);
   set(horder,'Position',[w-210,h-150,190,20]);
   set(horderval,'Position',[w-240,h-150,20,20]);
end
```

```
uiwait(gcf);

end
```

Appendix G

MatLab code to produce a scatter plot of (e.g. pink) L*a*b pixels from an RGB single colour image, as described in Chapter Three

This code was written by Louise Garner

```
labImage = rgb2lab(Pink);

LImage = labImage(:, :, 1);

aImage = labImage(:, :, 2);

bImage = labImage(:, :, 3);


a = size(aImage);

b = size(bImage);

aimagepixels = reshape(aImage, [a(1) *a(2),1]);

bimagepixels = reshape(bImage, [b(1) *b(2),1]);


figure;

scatter(aimagepixels,bimagepixels,'marker','.','MarkerEdgeColor',[1 0.600000023841858
0.7843137383461]);

xlim([0 50]);

ylim([0 50]);


xlabel('*a colour value','fontsize',20);

ylabel('*b colour value','fontsize',20);

ax = gca;

ax.FontSize = 18;

box off
```

```
maximuma=max(aimagepixels(aimagepixels>0))
minimuma=min(aimagepixels(aimagepixels>0))
maximumb=max(bimagepixels(bimagepixels>0))
minimumb=min(bimagepixels(bimagepixels>0))

arange=maximuma+minimuma;
midpointa=arange/2

brange=maximumb+minimumb;
midpointb=brange/2

meana=mean(aimagepixels(aimagepixels>0))
meanb=mean(bimagepixels(bimagepixels>0)
```

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