Non-invasive Technical Analysis of Illuminated Manuscript Leaves from the W.D. Jordan Rare Book and Special Collections, Queen's University: A Collaborative Project

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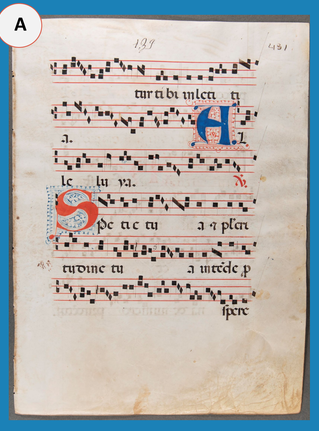
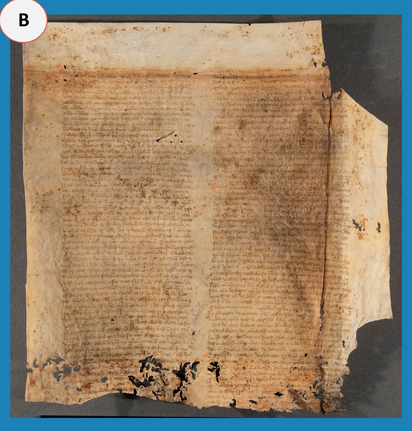
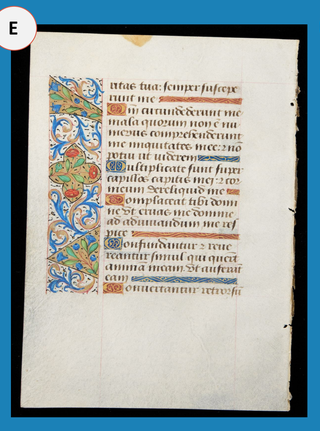
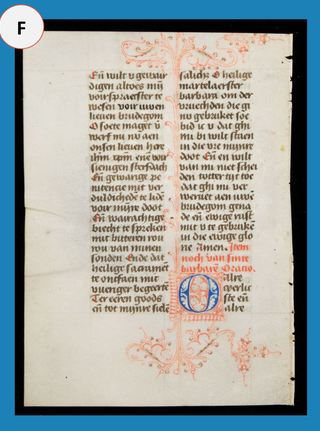
INTRODUCTION

In recent years, there has been a surge of technical analysis executed on illuminated manuscripts in order to enhance the understanding of the materials and techniques used to create them. The number of manuscripts that have survived due to their lack of exposure to the elements and human intervention has made them great sources of information to study artist materials used in certain time periods. This study focused on the non-invasive analysis of six manuscript leaves from the W.D. Jordan Rare Book and Special Collections at Queen's University. The goal was not only to identify the materials used to create the manuscripts but also to determine if the materials used were consistent with the time frame to which they are attributed. A secondary goal was to create a database of external reflectance spectra for the FTIR library of artists materials that can be used in future research.









- A — Choir Leaf, Normal Light, Recto
- B — Legal Treatise, Normal Light, Recto
- C — The Visitation, Normal Light, Recto
- D — Horae B.V.M, Normal Light, Recto
- E — Book of Hours, Normal Light, Recto
- F — Dutch Choir Leaf, Normal Light, Recto

EXPERIMENTAL

1. Preparation of standards was completed (see standard preparation section)
2. Microscopic observations using the Hirox RH 2000 at two different magnifications was completed to determine the homogeneity and density of pigments of the spots analyzed
3. Multispectral Imaging using the VSC 8000 was used to determine pigment distribution, ideal spots to analyze as well as make observations not seen with the naked eye
4. X-Ray Fluorescence (XRF) using the Bruker Tracer 5g to conduct elemental analysis was used on three spots of each color on each of the leaves
5. Fourier Transform Infrared Spectroscopy (FTIR) with External Reflectance ConservatIR attachment was used on the same three spots as XRF to determine chemical structure and possible identification of colorant

STANDARD PREPARATION

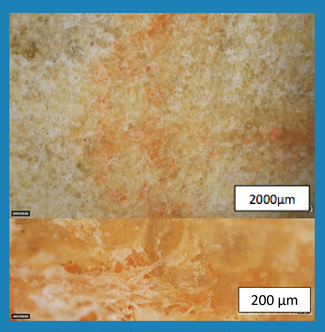
Colorant standards were prepared using two different methods. The first standards were made on parchment with ground pigments and one of two binders: glair or gum Arabic. Different amounts of each binder were used for each pigment in order to get the best consistency before brushing it on the parchment. The second standard was pure pigment pressed onto IR transparent SiC sandpaper. Proper safety procedures were followed for all pigment handling.

Standards on parchment

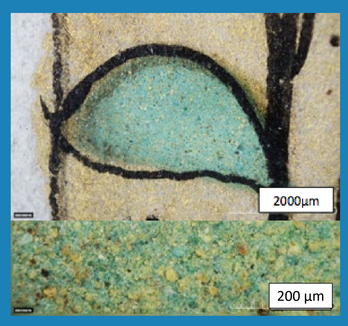
A few standard samples on SiC sandpaper

RESULTS

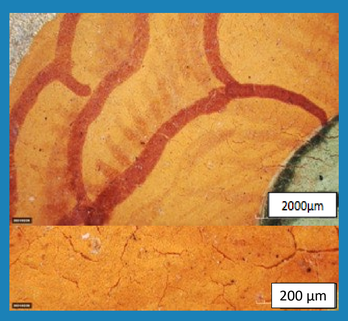
Observations made with the Hirox showed the density and homogeneity of the colorants on parchment. The choir leaf had a much higher density of pigment than the legal treatise which affected XRF and FTIR analysis. The higher density pigments made for larger intensity peaks in XRF and more distinctive peaks in the FTIR spectra. In the more illuminated manuscripts including the Visitation as well as the other Book of Hour leaves, mixtures of multiple pigments could be seen which help inform the interpretation of the XRF and FTIR data.



Legal Treatise. Light red lettering

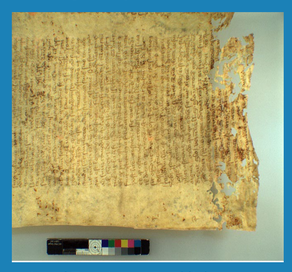


The Visitation. Mixture of green, blue, yellow

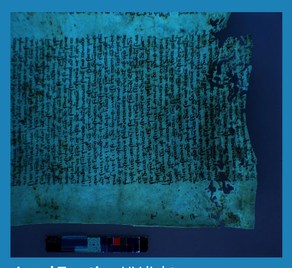


Horae B.V.M. Thick application of orange paint

Multispectral imaging helped not only to observe the pigment distribution and reveal details that could not be seen with normal light, but also helped in the identification of the pigments used. The blue pigment absorbed while the red reflected IR which is consistent with azurite and vermillion respectively. UV imaging of the legal treatise allowed for better legibility of the faded ink.



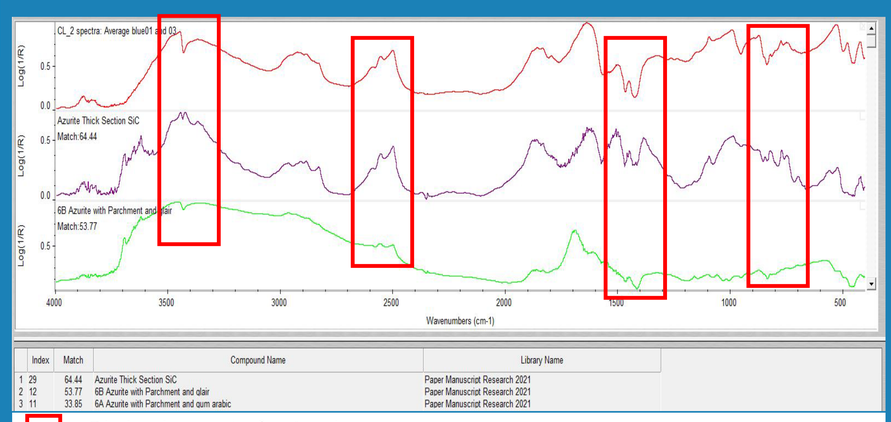
Legal Treatise, normal light



Legal Treatise, UV light

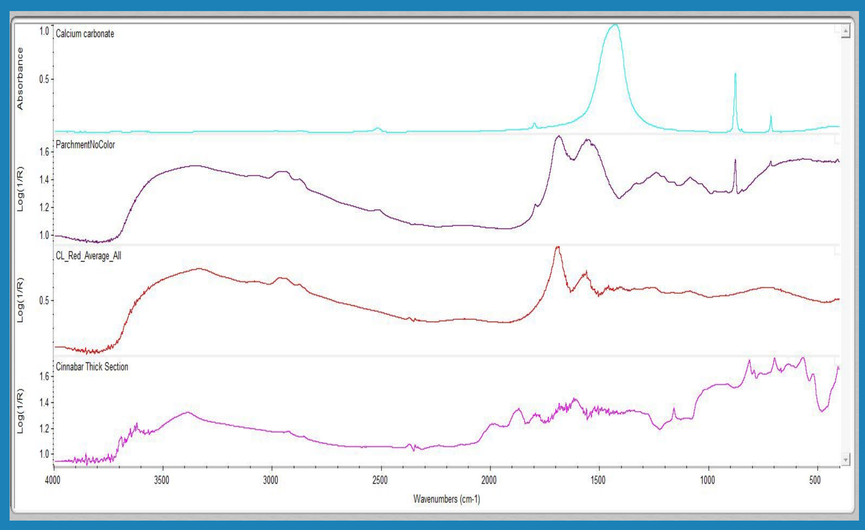
Horae B.V.M. Details showing the difference of the drypoint and reflective behaviour of the red colorant under normal light and infrared (725 nm).

XRF and FTIR Results					
Color	**Manuscript Leaves**	**Elements**	**Possible Pigments Identification (XRF)**	**FTIR Library Match**	**Comments**
White	Horae B.V.M	**Pb**, Cu, Ca, Au, S	Lead white ($2PbCO_3 \cdot Pb(OH)_2$)	Lead white on SiC	Clear match in IR database
Dark and pale green	Horae B.V.M Book of Hours	**Pb**, **Cu**, Ca, Au, S	Malachite ($Cu_2CO_3(OH)_2$) or verdigris ($Cu_2(OH)_3Cl$) mixed with lead-tin yellow (Pb_2SnO_4)	Malachite and gum Arabic on parchment Carmine in gum Arabic on parchment	Greens were often a mixture (yellow, blue and green) and not all components could be easily IDed with IR, hence the different library matches.
Gold	Horae B.V. M. Book of Hours	**Pb, Ca**, **Au**, Sn, S	Mosaic gold (tin sulfide)	Shell gold on parchment	Spectra was noisy probably due to the highly reflective nature of the gold
Orange	Horae B.V.M	**Pb**, **As**, Ca, Au, Cu, Sn, S	Lead-based pigment (red lead or realgar (?))	Iron gall ink on parchment	Limited library, no red lead or realgar sample was available
Black	Horae B.V. M Book of Hours.	**Ca**, Cu, As	Organic, carbon black	Iron gall ink on parchment	Limited library, no carbon ink sample was collected
Blue	All but the legal treatise	**Cu**, Ca, Au, Pb, Sn, S	Azurite ($Cu_3(CO_3)_2(OH)_2$)	Azurite on parchment or SiC sandpaper	Very clear match across leaves
Red	All Book of Hours	**Pb**, Ca, Cu, Au, S, Hg Ca, Fe, Zn	Vermilion/cinnabar (HgS) Iron Oxide	Parchment with glair plus others	Vermillion is not sensitive in IR, so the matches in FTIR were low. Iron oxide may have been IDed in the Book Hours leaf
Yellow	Horae B.V. M.	**Pb**, Ca, Cu, Au, Sn, S	Lead-tin yellow (Pb_2SnO_4)	Orpiment with glair on parchment	Tentative ID of Lead Tin Yellow when comparing absorption spectra with ER-IR spectra collected
Pink	The Visitation	**Pb**, Cu, S, Fe, Au	Calcium sulfate, organic red	Consistent with other organic reds from other leaves	
Purple	The Visitation	**Pb**, S, Cu, Ca, Au	Azurite and lead white	Lead white on SiC sandpaper	Matches white seen on other leaves, Most likely a mixture of white, blue and red
Ink	All	**Ca**, Pb, Fe	Iron gall ink ($FeSO_4$)	Logwood and glair on parchment, iron gall ink	Iron gall not as sensitive in the IR range, confirmed in literature
Parchment	All	**Ca**	N/A	N/A	N/A

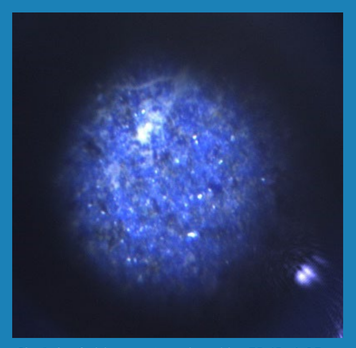


Distinctive peaks for Azurite

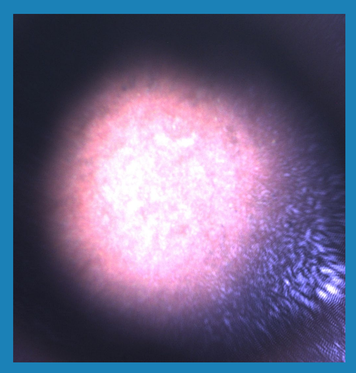
Choir leaf, average blue spectrum compared to Azurite on SiC Sandpaper and Azurite on Parchment with glair with distinctive peaks highlighted



Choir leaf, average red spectrum compared to parchment alone, calcium carbonate, and cinnabar standard on SiC sandpaper.



Choir leaf, blue spot analyzed by ER-IR, 1.25mm



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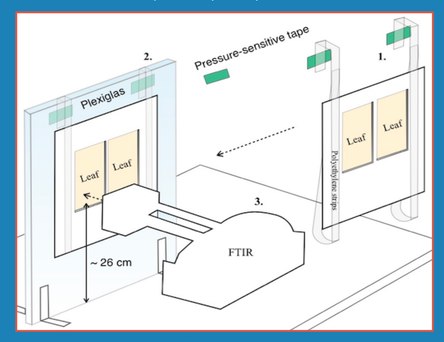

Diagram of ConservatIR Set-up

CONCLUSION

Due to the identification of azurite, vermillion/cinnabar, and iron gall ink in leaves, it was concluded that they are consistent with the time frame in which the manuscripts are attributed. The ConservatIR was able to collect clean and consistent spectra across the manuscripts and standards. Furthermore, the Reflectance FTIR database has a solid foundation of artists' pigments. Multispectral imaging allowed for increase legibility of legal treatise, which may be of use to future researchers for translations. In order to expand on our current results, it would be great if we could used Raman spectroscopy to help identify some of the colorants that are not sensitive in the Mid-IR range.

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