

Micro-XRF investigations of Books of Hours: Analyses of blue pigments in illuminated manuscript leaves from Books of Hours made in France in the 15th century



Application Note

Archaeology XGT41

Abstract: This application note introduces findings from the analyses of two illuminated manuscript leaves in the collection of the Yoshino Gypsum Art Foundation (hereafter referred to as “the Foundation”) using a HORIBA XGT-9000 X-ray Analytical Microscope. Among the Foundation’s elemental analysis investigations into the pigments used in the two leaves, this application note highlights the analysis results of the blue pigments and also the interpretation on the results. The interpretation is quoted from the Foundation’s publication [1].

Keywords: Cultural heritage, Art, Pigment analysis, Illuminated manuscripts, Micro-XRF

Introduction

X-ray fluorescence (XRF) is a non-destructive method for elemental composition determination of a material. XRF analysis determines the elemental composition by irradiating primary X-rays to a sample and by detecting the energies of fluorescent (secondary) X-rays released from the elements inside the sample. Among XRF analyzers, micro-XRF is a XRF analyzer equipped with X-ray optics such as a capillary to make X-ray beam into micro-spot, and it allows micro-area analysis on a sample. Micro-XRF also allows elemental distribution imaging by scanning a sample. Therefore, it is helpful for investigation of valuable paintings, artworks, and cultural assets which require non-destructive analytical approaches.

HORIBA XGT-9000 X-ray Analytical Microscope

The XGT-9000 X-ray Analytical Microscope (Figure 1) can perform micro-area analysis by micro-spot of X-ray beam down to 10 μm using the capillary optics. The XGT-9000 allows sample observation by a CMOS camera, irradiates the X-ray beam vertically from upper side of a sample, and detects fluorescent X-rays by a silicon drift detector (SDD) placed above. The XGT-9000 is equipped with a motorized stage, and it allows elemental distribution information within a sample by scanning the stage during XRF analysis.

Sample information

The samples are the two illuminated manuscript leaves shown in Figure 2 (a) and 3 (a), which are owned by the Foundation. Figure 2 (a) is a leaf with a miniature depicting Saint Sebastian (hereafter “the Saint Sebastian leaf”), and Figure 3 (a) is a leaf with a miniature depicting King David (hereafter “the Kind David leaf”).

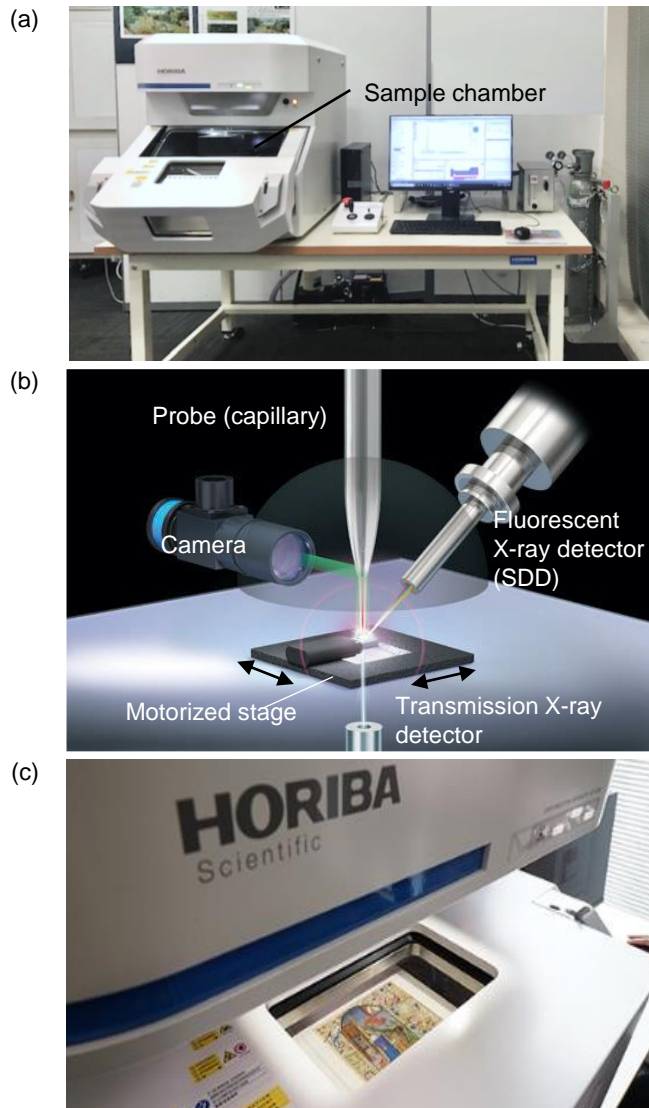


Figure 1 (a) Instrument set-up of the XGT-9000 (b) Schematic diagram of the optics (c) Sample setting in the sample chamber.

They are from two different 15th century French Books of Hours. The details are provided in the captions of Figure 2 and 3. Illuminated manuscripts are handwritten books in which the pages are decorated with precious metals such as gold and silver, and various colored pigments and dyes. Most of them have miniatures [1]. Illuminated manuscripts in general were damaged for various reasons [2]. Therefore, they often exist not as whole books but as single page leaves. For the reason, elemental analysis of pigments is one of the most effective ways to get the information of illuminated manuscript leaves that have been discovered, such as their original books, their production dates and places, the artists who painted them, and the patrons commissioning the illuminated manuscripts.

Measurement

Elemental distribution imaging was performed within the area enclosed by white line in Figure 2 (a) and 3 (a) with irradiating X-ray beam with a diameter of 100 μm . To avoid damage to the artwork, the analysis was conducted under a partial vacuum condition, where only the optical

area was kept in a vacuum stage and the sample chamber was kept in an atmospheric state.

Result – Blue pigment identification

Although blue is used for the sky in both illuminated manuscript leaves, the analysis detected different elements. As shown in Figure 2 (b), Al and Si were found in the blue sky of the Saint Sebastian leaf, while Cu was detected in the blue sky of the King David leaf as shown in Figure 3 (b).

The Foundation's investigation report (2022) suggested that Al and Si may be contained in lazulite ($\text{Na}_6\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_2$), the main element of lapis lazuli which is thought to have been difficult to obtain and expensive at the time the illuminated manuscripts were painted, and that Cu may be contained in a mineral called azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), which was relatively easier to obtain and inexpensive in those days [1][3]. The analysis results indicate that lapis lazuli and azurite may have been used in the blue sky areas of the two illuminated manuscript leaves.

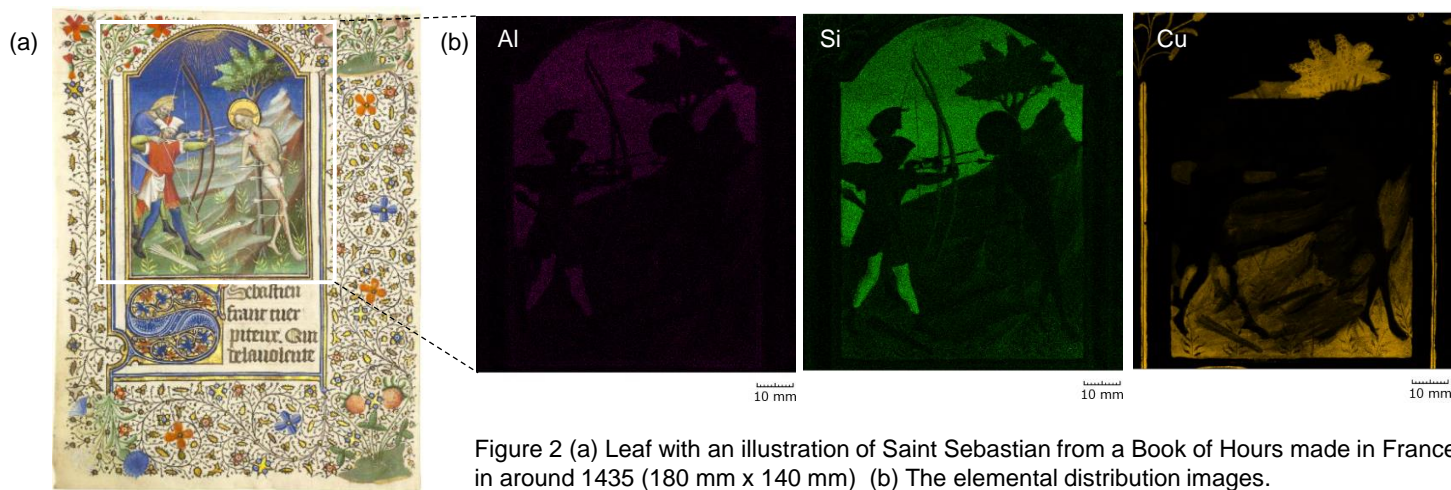


Figure 2 (a) Leaf with an illustration of Saint Sebastian from a Book of Hours made in France in around 1435 (180 mm x 140 mm) (b) The elemental distribution images.

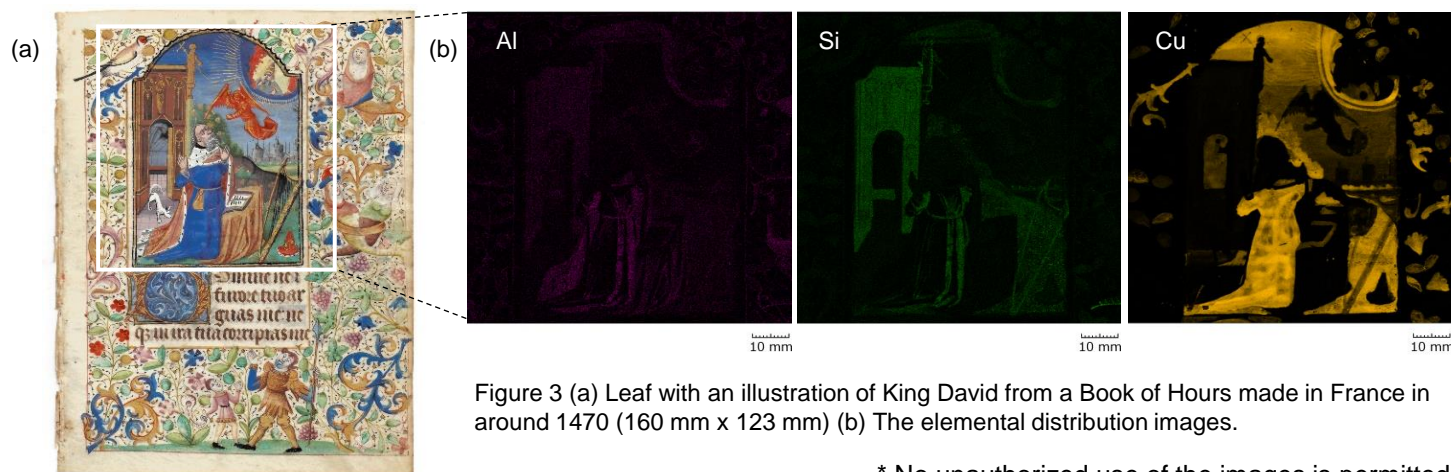


Figure 3 (a) Leaf with an illustration of King David from a Book of Hours made in France in around 1470 (160 mm x 123 mm) (b) The elemental distribution images.

* No unauthorized use of the images is permitted.

Conclusion

The elemental analysis results obtained by the XGT-9000 X-ray Analytical Microscope showed that different elements were detected in the blue sky areas of the two illuminated manuscript leaves. It suggested that different pigments were used and that they were possibly lapis lazuli and azurite [1].

In this way, micro-XRF potentially contributes, as a non-destructive elemental analysis technique, to investigations of artworks such as illuminated manuscripts.

Acknowledgement

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For more details, please see the following research report: Yuki Nishida, A historical study on two 15th century illuminated manuscript leaves in Yoshino Gypsum Art Foundation through pigment analysis. *Yoshino Gypsum Art Foundation Bulletin*. no.4 (2022), p.33-50.

References

- [1] Y. Nishida, A historical study on two 15th century illuminated manuscript leaves in Yoshino Gypsum Art Foundation through pigment analysis. *Yoshino Gypsum Art Foundation Bulletin*. no.4 (2022), p.33-50.
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Learn more about the story via the interview

[HORIBA Talk - "Unravelling History: Pigment Analysis of Illuminated Manuscript Leaves"](#)

