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CONFOCAL X-RAY FLUORESCENCE MICROSCOPY FOR THE ANALYSIS OF PAINTINGS: CASE STUDY OF *THE ARMORER'S SHOP*

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ABSTRACT

The 17th c. Flemish painting on panel, The Armorer's Shop, has long been attributed to David Teniers the Younger (1610-1690). The painting was found to have an unusual construction whereby the lower corner of the panel appeared to be a separate smaller panel that had been incorporated into the overall larger panel. This prompted further investigation using a broad range of materials analysis techniques, particularly cross-sectional analysis, dendrochronology, and confocal x-ray fluorescence microscopy (CXRF), a non-invasive technique that utilizes specialized x-ray optics that allow x-ray fluorescence data to be obtained as a function of depth. Stylistic analysis and art historical research led to the attribution of Jan Breughel the Younger as the probable artist of the initial, smaller panel. Scientific analysis supports the hypothesis that the smaller panel was painted first then incorporated into the overall panel. In particular, CXRF revealed the composition and location of buried paint layers at the panel interfaces by combining depth scans at a number of adjacent lateral positions to produce virtual cross-sections over 20 mm in length. The relationship of the paint layers at the panel interfaces provided evidence for the armor panel having been painted separately and prior to the rest of the composition. This data, along with dendrochronological and IRR data, provided a chronology of construction for the painting that offered additional evidence for a Brueghel attribution. This study highlights the importance of a multidisciplinary approach for the analysis of paintings, as well as the advantages of non-invasive techniques, such as CXRF analysis, which allow for a comprehensive survey of the paint layer structure throughout the painting. An overview of the CXRF technique will be provided along with a discussion of how CXRF data relates to data collected using SEM-EDS, FTIR, Raman, conventional XRF, x-radiography, IRR, and dendrochronology.

INTRODUCTION

Noninvasive techniques offer a great advantage in the scientific investigation of art and other cultural artifacts, particularly when used to expand upon results from conventional analysis. Confocal x-ray fluorescence (CXRF), or 3D micro-XRF, is a non invasive technique that combines two x-ray focusing optics in a confocal arrangement to resolve x-ray fluorescence from a particular, 3D volume in space. The strength of this technique is that the elemental make up of the sample can be determined as a function of depth, and it has already successfully employed for the investigation of paint and paintings [1-8].

Figure 1. *The Armorer's Shop, attributed to David Teniers the Younger, 56.5×80.7 cm², oil on panel, NCMA. The long solid lines indicate the interface between the armor-containing plank and the remainder of the panel. The dashed line indicates a third join discovered during dendrochronological analysis. The short lines indicate the locations of confocal XRF scans across the interface. The numbered arrows show the locations of samples used for conventional microanalysis.*

The importance of the use of non-invasive techniques for holisitic examination in conjunction with conventional microanalysis methods is evidenced by the analysis of *The Armorer's Shop*, a Flemish painting attributed to David Teniers the Younger (1610-1690). The painting is an oil on panel which depicts a seated armorer and a richly detailed pile of parade armor in front of a figural grouping of workers at a forge. During routine examination of the painting, the panel was found to have a highly unusual construction, whereby the parade armor in the lower left corner is painted on its own distinct plank. This smaller panel was incorporated into a larger work on panel, and the two perpendicular joins of this construction are indicated by the solid white lines in figure 1. Both joins are visible as raised ridges in raking light, as well as by transmission radiography (not shown). Additionally, both x-radiography and IRR examination of the painting revealed several compositional changes in the armor panel, further supporting the notion that this panel was incorporated into the overall composition of the painting.

Art historical investigation led to the discovery that the armor pile in figure 1 is nearly identical to armor in at least six other paintings, all but one of which are attributed to Jan Brueghel the Younger (1601-1678). While there is historical evidence that there were collaborative projects between Teniers and Brueghel [9-10], no examples of such work have been firmly identified. Collaboration among two or more painters was common practice among Northern European painters in the 17th century [9], this painting, constructed by the incorporation of an already-painted single panel into a larger scene, is unique. Moreover, it is unclear whether the term 'collaboration' should be applied to this work at all. This paper will summarize the multifaceted investigation of the construction, composition, and palette of *The Armorer's Shop*, highlighting the importance the non-invasive technique CXRF.

EXPERIMENTAL

Fourier transform infrared microspectroscopy (FTIR) was performed using a Thermo-Nicolet Magna 560 IR spectrometer with a Nicolet Nic-Plan microscope in transmission mode. For each sample (mounted on a diamond half-cell) 128 scans were acquired from 4000 cm^{-1} to 650 cm^{-1} at a spectral resolution of 4 cm^{-1}. Spectra were collected with Omnic E.S.P. 6.1a software and analyzed using the Infrared and Raman Users Group (IRUG) database and commercial polymer and organic chemical libraries. Non-destructive, qualitative energy dispersive XRF was performed using a Bruker ArtTAX μXRF spectrometer with a molybdenum tube operated at 50 kV, 600 microamps, and 200s collection time. A polycapillary focusing optic was used to achieve an approximately 70 micron incident beam size, and Intax version 4.5.18.1 software was used to interpret spectra. Scanning electron microscopy was conducted with a Topcon ABT 60 SEM operated at 20 kV, a 22 mm stage height and a 20 degree sample tilt. Paint layer thicknesses from SEM images were calibrated and measured using ImageProPlus software (Media Cybernetics). Energy dispersive x-ray spectra were collected using an EDAX x-ray detector, an Evex pulse processor and multi-channel analyzer, and Evex Nanoanalysis software. Raman spectroscopy was performed on a Renishaw inVia Raman spectrometer using a 785 nm diode laser, a 50x objective, 1200 l/mm grating, a laser power of 3 mW at the sample, a spectral range of 100 cm^{-1} to 3200 cm^{-1}, and a spectral resolution of 1 cm^{-1}/CCD pixel (functional resolution of 3 cm^{-1}). Data was also collected using a JY Horiba LabRAM Aramis Raman spectrometer with a 50x objective, 785 and 633 nm lasers, a laser power of 8 mW at the sample, a 1200 l/mm grating, a spectral range of 200 cm^{-1} to 1600 cm^{-1}, and a spectral resolution of 1 cm^{-1}/CCD pixel.

The CXRF experiments were carried out at CHESS station D1, using monochromatic radiation at 18 keV, selected using a 1% bandpass multilayer monochromator. A single-bounce monocapillary, fabricated at CHESS [11], was used to provide a focused incident beam of approximately $5x10^9$ photons/second into a 20 μm-diameter spot. A double-focusing polycapillary lens (X-ray Optical Systems) with an input acceptance angle of 25^o, was used to collect x-ray fluorescence from the sample and direct it onto a Rontec Xflash silicon drift detector. The detector resolution is approximately 0.16 keV. The two optics define a 3D sample volume as described previously [1]. The energy-dependent depth resolution with the setup used for the scans presented here varied smoothly from 31 μm at 4.5 keV to approximately 15 μm at 16 keV. The painting was mounted on a large-area, high resolution 3D scanning stage equipped with an easel-style mount [12]. To increase the distance between the painting and polycapillary lens, the sample surface was oriented 32^o from the incident beam, rather than 45^o, as in prior experiments.

For dendrochronology, one end of each plank in the support panel was prepared, and the widths of all rings were measured to 0.05 mm precision. The outer growth rings of the opposite ends were also prepared and measured, both to be sure that each plank's outermost ring was counted and to determine whether any sapwood rings were present (sapwood consists of the outer rings next to the bark: these rings are generally removed due to low durability, leaving just the heartwood). In addition, all edges of the panel were examined for structural and wood anatomical features. The data from each plank were compared with several established Baltic, German, and Dutch oak chronologies to determine the source of the wood and the outer ring dates of the planks, using standard dendrochronological statistical and visual techniques [13].

RESULTS AND DISCUSSION

Dendrochronology

Dendrochronological analysis revealed two unexpected features of the overall construction. First, the panel is comprised not of two, but of three separate planks, as illustrated in figure 2. Visual inspection indicated that the armor plank (plank 1 in figure 2) was glued onto the bottom plank (plank 2), which was evidently planed down expressly for this purpose and which extends the full width of the painting. To the authors' knowledge, such an insertion of one plank into another is unique to this panel [14]. The second unusual feature, also indicated in figure 2, is the unusual orientation of the bottom two planks relative to their ring-growth direction, where both bottom planks have their *outer* rings at the *outer* edge of the panel. Typically, the inner growth rings would be at the outer edge of the panel to maximize the strength of the construction [15]. The orientation of plank 2 was evidently chosen to match that of plank 1 to minimize damage due to warping. These observations both indicate that *The Armor's Shop* panel was conceived to make use of the pre-existing painting of armor on plank 1.

The outer rings of the two forge planks (planks 2 and 3 in figure 2) date to 1620 and 1624. Since these two planks were painted at the same time, the later date is used to estimate the painting date. The average of 15 sapwood rings (range of 9-23) plus 5 years between felling and painting (range of 2-8) gives a most likely date of 1644 or after for the completed work, with a statistically likely range of 1638-1652. In contrast, the outer ring of the armor plank dates to 1605, yielding a most likely painting date of 1625 and a probable range of 1619-1633. Thus, dendrochronological analysis suggests that the armor plank was painted approximately 20 years before the remainder of the painting [2].

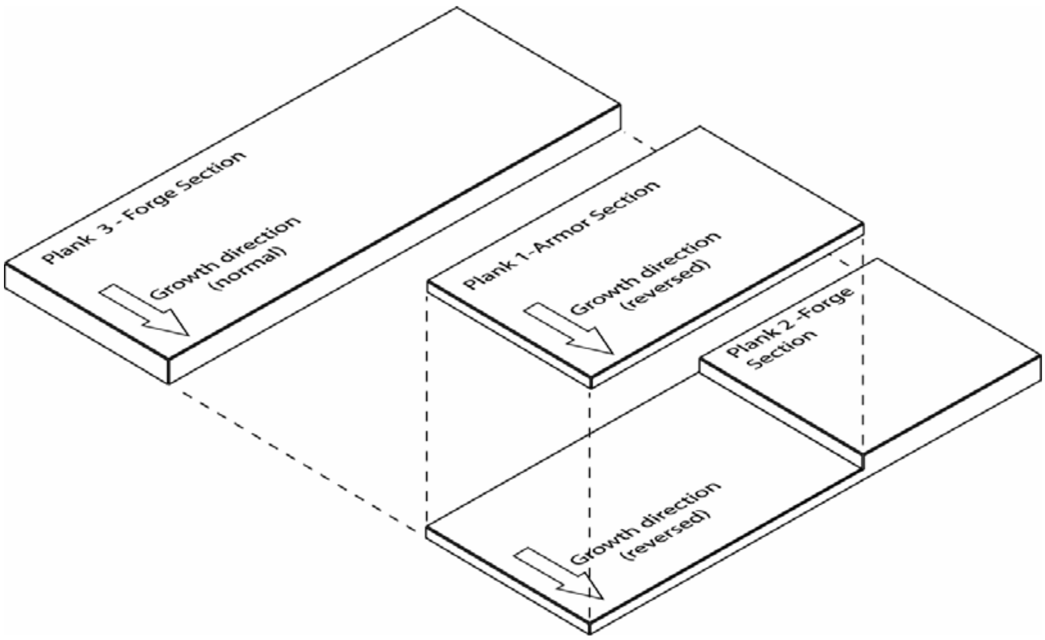

Figure 2. *Construction of The Armorer's Shop, as revealed by optical microscopy and dendrochronology. Arrows indicate the growth direction of each of the wood planks. For the bottom two planks, this growth direction is reversed compared to conventional practice, in which planks are oriented so that their older, harder wood faces outward.*

Conventional Analysis

Cross-sectional samples were studied with optical microscopy and SEM-EDS to evaluate the layer thicknesses and structures in different portions of the painting. Figure 3 shows a backscattered electron image of one of the cross-sections (sample 1). In visible light, all of the cross-sections contain an off-white, Ca-based ground with very fine particulation. Above this layer, figure 3 clearly shows a 2-10 micron layer consisting primarily of lead, identified as an imprimatura, and in samples 2, 15, and 18 also contained small amounts of copper.

The palette as determined from conventional XRF, FTIR and SEM-EDS analysis is consistent with a traditional 17th century palette throughout both sections of the painting: vermilion and iron oxide reds, lead-tin and iron ochre yellows, lead white, azurite blue, umber browns, flesh tones created by mixing lead white, vermilion, iron oxide reds, and umber [16-20]. In SEM/EDS, the identification of calcium and phosphorus together in the grey particles of the imprimatura layer in figure 3 is suggestive of bone black, and the identification of aluminum and silicon in the dark (low-Z) particles is suggestive of the clay minerals typically associated with iron ochres.

SEM/EDS results as well as the ubiquitous presence of lead and copper throughout the painting in XRF results as well as the presence of dark blue particles in visible microscopy suggest a lead white imprimatura with azurite, which was found in both sections of the painting. FTIR and Raman analysis on samples confirmed the presence of a chalk ground as well as lead white in a drying oil. The composition, number and thickness of paint layers, as well as the materials and construction of the ground and imprimatura are consistent with 17th century northern European painting practice [18, 21-22], but do not reveal any substantive differences between the armor and forge sections outlined in figure 1.

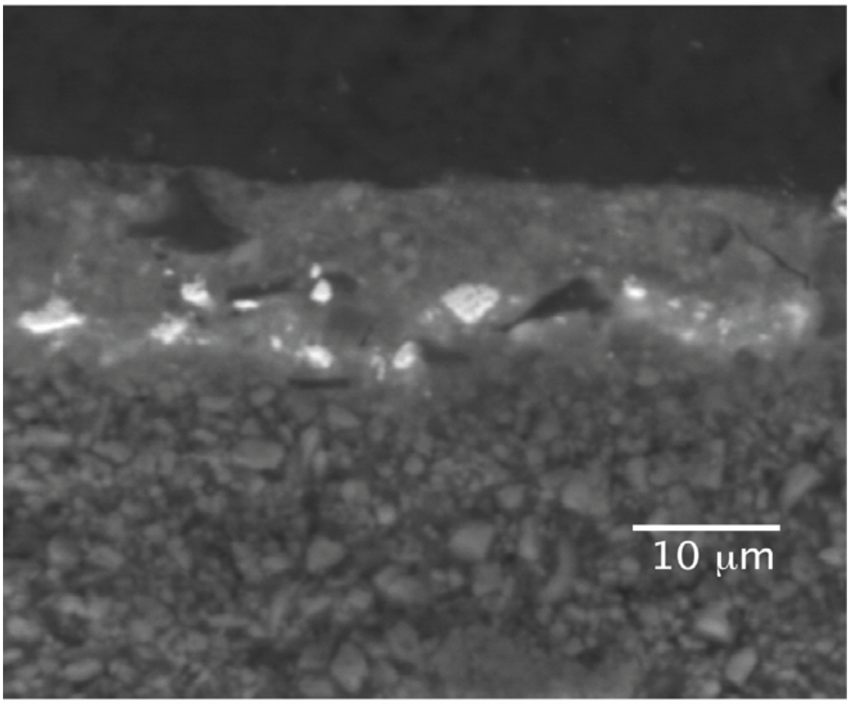

Figure 3. *Backscattered SEM image of sample 1 (see Fig. 1), taken from the grey area from the armor pile, showing the presence of a lead white-containing imprimatura layer. Magnification 2000X.*

Confocal X-Ray Fluorescence

In order to resolve the chronology of the painting's construction without further sampling, CXRF was used to scan multiple areas of the painting, focusing on areas near and across the join. Figure 4 shows a scan across the join (indicated by the blue arrow in figure 1). The location of the join can be seen by the sudden change in slope and height of the surface that makes the join visible under raking light. The most notable feature in this scan is the appearance of an additional buried paint layer, which is seen by the extra Pb Lα and Cu Kα peaks below the top layer. This buried layer begins at the join and slopes upward to the presentation surface in the armor section. This layer was found in each of the line scans across the join that are indicated in figure 1, and appears to be the imprimatura on the armor panel. When this panel was later incorporated into the larger panel, additional ground was applied material to smooth any gaps caused by height differences at the interface and then a new imprimatura and presentation surface, corresponding to the upper layer in figure 4, was applied to both sides of the join. In contrast, no buried layers were observed on the forge section, suggesting that this section was only painted after the join. Thus, the data show that the armor plank, and probably the armor itself was painted first, and that *The Armorer's Shop* composition was conceived to make use of this earlier image.

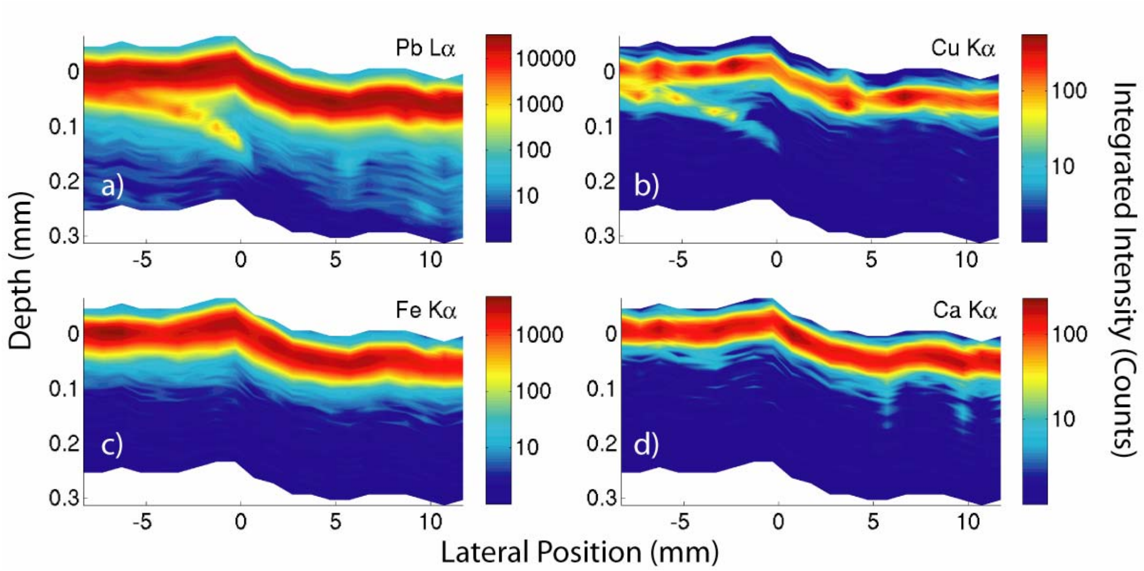

Figure 4*: Virtual cross-section across the interface between parts 1 and 2, showing an earlier imprimatura on part 1. The position of the line scan is indicated in Fig. 1. (a), (b), and (d) show the fluorescence intensity on a logarithmic color scale. (c) shows the Cu K[illegible] concentration on a linear scale.*

CONCLUSION

The wide variety of analysis techniques presented here each add insight to the construction and history of *The Armorer's Shop*. Holistic examination suggested that the armor is contained on a small, rectangular plank that was incorporated into a larger composition and that the armorer and forge sections of the work were painted by Teniers, while the armor plank was most likely painted by a different artist, possibly Jan Brueghel the Younger based on art historical evidence. Using CXRF provided direct evidence that the armor panel was painted before the complete panel was constructed by the appearance of a secondary paint layer believed to be an earlier imprimatura. While is was not possible to locate this layer in the micro-samples taken, conventional analysis on these samples provided detailed information on the paint layer structure and materials, verifying that they were consistent with 17th century Flemish oil paintings. Finally, dendrochronology shows that all three planks forming the panel were felled in the early 1600s, and that the armor plank was most likely painted 20 years before the other two planks. Here scientific investigation was used to support the art historical evidence that the armory panel was panted by a different artist, and in view of these results, in 2005 the attribution of *The Armorer's Shop* was changed to David Teniers the Younger and Jan Brueghel the Younger. This study highlights the primary advantage of non-invasive techniques, where the ability to depth profile multiple areas in the painting was critical in locating a key feature in the paintings construction.

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