Tracing the artist's intent

Combining micro- and macroscopic analysis with art technological sources to study 17th-century paintings

De Keyser, N.

Publication date
2025

Chapter: 6
Future perspectives

Future perspectives

The primary focus of this thesis has been to develop a methodology for gaining deeper insight into the original painting techniques and understanding the artist's intended appearance. However, the ultimate goal is to achieve a complete visual representation of the original intended appearance, making reconstruction-based research a logical next step. Despite progress, many open questions remain, complicating efforts to approximate a truly faithful reconstruction. These challenges include the precise characterization of material compositions, distinguishing original components from secondary products, and understanding the exact degradation pathways that have occurred over time.

A faithful reconstruction necessitates knowledge of the physicochemical and optical properties of the entire paint stratigraphy. Factors such as pigment volume concentration, mixture heterogeneity, particle size, and morphology significantly influence these properties but are challenging to determine accurately. Imaging modalities like macroscopic X-ray fluorescence (MA-XRF), macroscopic X-ray powder diffraction (MA-XRPD), and reflectance imaging spectroscopy (RIS), along with traditional microscale analysis of paint cross-sections, provide critical insights but have inherent limitations.

6.1 Strengths and Limitations of Imaging Modalities

6.1.1 Macroscopic X-Ray Fluorescence (MA-XRF)

MA-XRF allows for elemental mapping of artists' materials, revealing the distribution of elements both on the surface and deeper within the object's stratigraphy. This technique offers insights into compositional changes and the artist's creative process. However, it cannot quantify paint stratigraphy due to matrix absorption phenomena, which can reduce detection sensitivity for deeper layers and low atomic number elements. Additionally, secondary fluorescence effects may lead to overestimations of certain elements. While MA-XRF and combined confocal XRF can provide qualitative stratigraphic information about elemental distributions [1,2], deriving semi-quantitative values for layer composition and thickness remains complex for multi-layered heterogeneous paintings.

6.1.2 Macroscopic X-Ray Powder Diffraction (MA-XRPD)

MA-XRPD offers detailed information about crystalline pigment phases and degradation products. The capabilities of MA-XRPD for providing quantitative information of pigments has been demonstrated [3–5], as well as its potential to differentiate crystallite sizes of pigments based on the FWHM (full width at half maximum) of the measured diffraction peaks [6,7], which could be leveraged more to differentiate *in-situ* formed (nano-like) compounds from original pigments. However, MA-XRPD is limited to superficial paint layers when operating in reflection mode, with probing depths varying by paint matrix. While transmission mode can obtain quantitative information on the ground layer, it is less sensitive to superficial compounds in thin layers. Depth-selective possibilities of MA-XRPD in transmission mode has been demonstrated on a fifteenth-century illuminated parchment, by exploiting the shift of the measured diffraction peaks with respect to reference data, however, the ability to determine absolute displacements for different compounds in a layered sample is a challenge for the non-invasive analysis of real objects and is depended on how well the actual unit cell dimensions of the materials inside the object are known [8].

6.1.3 Reflectance Imaging Spectroscopy (RIS)

RIS-VNIR captures spectral signatures of pigments at the paint surface, offering insights based on electronic transitions related to material color. The technique complements MA-XRF and MA-XRPD but struggles with pigments such as yellow lakes affected by degradation due to spectral feature loss. Emerging high-sensitivity molecular fluorescence imaging spectroscopy (FIS) shows promise for addressing these challenges, as demonstrated with red lakes, but requires further exploration for more pigments such as the challenging faded yellow lakes [9,10]. Other limitations of RIS are also the non-linear mixing effects complicating pigment identification.

6.1.4 Cross-Section Analysis and Advanced Techniques

For detailed stratigraphic information, cross-section analysis using techniques like light microscopy, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX), and micro-Raman spectroscopy remains essential. However, these methods are limited to analyzing the visible surface plane of cross-sections, providing only partial insights into pigment particle morphology, size, and distribution. Recent advances, such as synchrotron (SR)-based correlated X-ray fluorescence and X-ray ptychography nano-tomography, have demonstrated potential for 3D characterization. These techniques allow visualization of the organic fraction and low atomic number components of the paint, offering a more comprehensive understanding of the stratigraphy and pigment composition [11].

6.2 Enhancing Imaging Modalities and Data Integration

Future research should focus on expanding the capabilities of imaging modalities and overcoming their limitations. Improvements in data processing [12], registration, and fusion are essential for integrating complementary information from the various (imaging) techniques. Machine learning algorithms have shown promise in improving data processing, particularly for MA-XRF [13], improving the accuracy in quantifying fluorescence line intensities under low-count scenarios, and RIS datasets [14], for an automated and more accurate pigment classification, outperforming techniques like the spectral angle mapping algorithm. Recently, data fusion of MA-XRPD with MA-XRF and RIS was used to overcome the time consuming nature and lower resolution of MA-XRPD maps [15,16]

6.3 Reconstruction-Based Research

Also reconstruction-based research with historically appropriate materials, in mixtures or layers have proven specifically useful to better understand the detection limits of the imaging modalities [12,17] Specifically the use of mock-ups and/or mimicked build-up and paint stratigraphy. Recently, for instance, by combining RIS-VNIR (400 to 1000nm, more sensitive to the surface) and RIS-SWIR (900 to 2500nm, penetrating deeper into the paint layer), leveraging different spectral penetration depths, with MA-XRF scanning in conjunction with paint mock-ups, the nature of the Cu-containing materials (as a pigment or a drier) and their use in underlayers could be discriminated in works by Vermeer [17].

Further exploration of the non-invasive imaging modalities, coupled with 3D characterization and predictive modeling, will be critical for advancing our understanding of historical artworks. Characterizing reconstructions before and after aging with multimodal techniques (MA-XRF, MA-XRPD, RIS, cross-section analysis) could build comprehensive reference datasets. These datasets may ultimately enable machine learning models to predict how paintings age and evolve, aiding in approximating the original intended appearance despite complex degradation processes (Fig. 6.1).

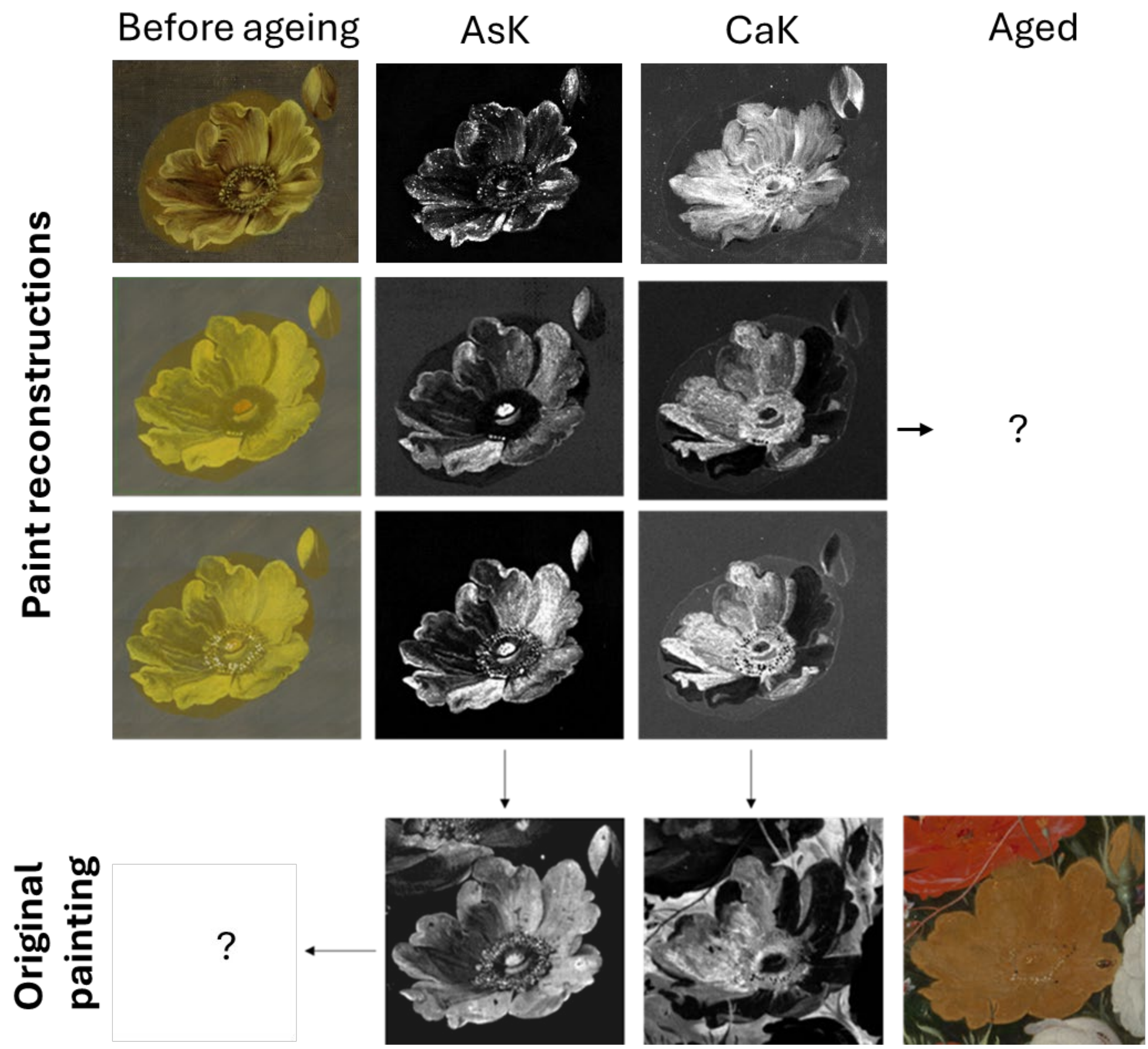

Fig. 6.1 Predicting change based on historically Accurate Reconstruction Techniques: Insight into the original intended appearance of Mignon's yellow rose and evaluating further ageing mechanisms.

6.4 References

1. Trojek T, Prokeš R, Šefců R, Bilavčíková H, Čechák T. Confocal X-ray fluorescence spectrometer for in-situ analyses of paintings. Radiat Phys Chem. 2017;137:238–42.

2. Lachmann T, Van Der Snickt G, Haschke M, Mantouvalou I. Combined 1D, 2D and 3D micro-XRF techniques for the analysis of illuminated manuscripts. J Anal At Spectrom. 2016;31:1989–97.

3. De Meyer S, Vanmeert F, Vertongen R, van Loon A, Gonzalez V, Delaney J, et al. Macroscopic x-ray powder diffraction imaging reveals Vermeer's discriminating use of lead white pigments in Girl with a Pearl Earring. Sci Adv. 2019;5:eaax1975.

4. Vanmeert F, van Loon, Annelies, Gabrieli F, Krekeler A, Verslype I, De Meyer S, et al. Discerning variations in Vermeer's ultramarine blue utilizing MA-XRF, RIS, and MA-XRPD. X-ray fluorescence imaging (MA-XRF) and reflectance imaging spectroscopy (RIS) 2024 meeting. 7 Jun 2024; Washinton D.C.

5. Vanmeert F, Hendriks E, Van der Snickt G, Monico L, Dik J, Janssens K. Chemical Mapping by Macroscopic X-ray Powder Diffraction (MA-XRPD) of Van Gogh's Sunflowers: Identification of Areas with Higher Degradation Risk. Angew Chem Int Ed. 2018;57:7418–22.

6. Vanmeert F. Highly specific X-ray powder diffraction imaging at the macroscopic and microscopic scale[PhD thesis]. Antwerp: University of Antwerp; 2019.

7. De Meyer S. Macroscopic X-ray Powder Diffraction in Reflection Mode: A New Technique for Chemical Imaging of Artworks[PhD thesis]. Antwerp: University of Antwerpe; 2023.

8. Vanmeert F, De Nolf W, Dik J, Janssens K. Macroscopic X-ray Powder Diffraction Scanning: Possibilities for Quantitative and Depth-Selective Parchment Analysis. Anal Chem. 2018;90:6445–52.

9. Dooley KA, Chieli A, Romani A, Legrand S, Miliani C, Janssens K, et al. Molecular Fluorescence Imaging Spectroscopy for Mapping Low Concentrations of Red Lake Pigments: Van Gogh's Painting The Olive Orchard. Angew Chem Int Ed. 2020;59:6046–53.

10. Delaney JK, Dooley KA, van Loon A, Vandivere A. Mapping the pigment distribution of Vermeer's Girl with a Pearl Earring. Herit Sci. 2020;8:4.

11. Broers FTH, Verslype I, Bossers KW, Vanmeert F, Gonzalez V, Garrevoet J, et al. Correlated x-ray fluorescence and ptychographic nano-tomography on Rembrandt's The Night Watch reveals unknown lead "layer." Sci Adv. 2023;9:eadj9394.

12. De Almeida Nieto LM, Gabrieli F, Van Loon A, Gonzalez V, Dik J, Van De Plas R, et al. Comparison of macro x-ray fluorescence and reflectance imaging spectroscopy for the semi-quantitative- analysis of pigments in easel paintings: A study on lead white and blue verditer. X-Ray Spectrom. 2024;53:438–51.

13. Preisler Z, Andolina R, Busacca A, Caliri C, Miliani C, Romano FP. Deep learning for enhanced spectral analysis of MA-XRF datasets of paintings. Sci Adv. 2024;10(39):eadp6234.

14. Pouyet E, Miteva T, Rohani N, de Viguerie L. Artificial Intelligence for Pigment Classification Task in the Short-Wave Infrared Range. Sensors. 2021;21:6150.

15. Gestels A. Prediction of quantitative MA-XRPD distributions using data from hyperspectral methods. X-ray fluorescence imaging (MA-XRF) and reflectance imaging spectroscopy (RIS) 2024 meeting. 7 Jun 2024; Washinton D.C.

16. Gestels A, Gabrieli F, De Kerf T, Vanmeert F, García HF, Delaney J, et al. High-resolution compound-specific mapping in works of art via data fusion of MA-XRPD with hyperspectral data (part 1: Method evaluation). Talanta. 2024;280:126731.

17. Gabrieli F. Through Vermeer's paint layers: RIS and MA-XRF for a non-invasive understanding of the use of copper. X-ray fluorescence imaging (MA-XRF) and reflectance imaging spectroscopy (RIS) 2024 meeting. 7 Jun 2024; Washinton D.C.