Underneath the surface

Advanced synchrotron techniques for the study of 17th century oil paint in three dimensions

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Publication date
2025

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Conclusions and outlook

"Art is never finished, only abandoned."
- Leonardo da Vinci (?)

6.1 Conclusions

The goal of the work reported in this thesis was to explore what advanced synchrotron techniques, and specifically tomographic techniques, can add to the understanding of 17th century paint and paint degradation. Paintings have a complex stratigraphy and have a very heterogenous composition containing both organic and inorganic components. The three-dimensionality of paintings is an important factor to consider when studying the condition of the paint and the chemical reactions taking place in these centuries-old objects of art.

In **Chapter 2** the degradation pathway of the yellow orpiment (As_2S_3) was studied. To study the reaction, model samples were made and artificially aged. The formation of arsenic trioxide (As_2O_3) from orpiment due to light-induced degradation was confirmed by tomographic transmission X-ray microscopy (TXM) at several energies. The presence of arsenic trioxide was both verified via its chemical as well as its physical properties visualized by the 3D volume rendering, showing characteristically shaped arsenolite (As_2O_3) crystals. Although the TXM set-up showed potential of probing both the chemical and physical properties of pigments, the limited field of view (FOV) complicates upscaling to study larger historical paint samples. The degradation pathway was also confirmed by X-ray absorption near-edge spectroscopy (XANES). Both techniques did not show the presence of As(V)-species. In different model samples, in which the orpiment was aged in the proximity of a medium such as egg yolk, these As(V)-species were present. Measurements on an historical paint sample of *Still Life with Flowers in a Glass Vase* (1650–1683) by Jan Davidszn. De Heem confirmed the existence of two different degradation pathways, one in which orpiment in direct contact with light forms arsenic trioxide, and the second pathway in which the orpiment is partially dissolved (As(III)-OH type) and then forms As(V)-species. When these As(V)-species come into contact with lead ions, lead arsenates can form. The presence of a medium is necessary for the As(V)-species to form, which can then also form without any exposure to light. The measurements on the model samples enabled studying the degradation of orpiment in different controlled environments and thereby clarifying the different steps and pathways.

In **Chapter 3** the arsenic sulfide pigments present in *The Night Watch* were studied and characterized. This was done by analysis of two micrometric paint samples taken from two areas in the yellow costume of Willem van Ruytenburch, one of the two central figures of the famous painting by Rembrandt van Rijn. Unexpectedly, pararealgar and a semi-amorphous pararealgar were identified by micro-Raman spectroscopy. The hypothesis is that these two arsenic sulfides were used by Rembrandt as pigments to imitate gold, and pararealgar did not form as degradation product of the red realgar (As_4S_4). The hypothesis is supported by the discovery of a very similar paint mixture in orange paint in a still life painting by Willem Kalf, who also lived in Amsterdam in the mid 17th century. Historical sources show that a wide variety of arsenic sulfides, both natural and artificial, were available in 17th century Amsterdam. There were several pigment trading routes in Europe mentioning arsenic sulfides. These pigments have not been found in the oeuvre of Rembrandt before. The research emphasizes the importance of combining macroscale and microscale analytical approaches and shows how the study of historical sources can help to (dis)prove hypotheses based on scientific results while providing a broader context to the findings.

Another type of paint from *The Night Watch*, the unique quartz-clay ground, was studied in **Chapter 4**. In this chapter, synchrotron radiation-based (SR) correlated X-ray fluorescence and ptychographic nano-tomography was employed for the first time on an historical paint sample. The 3D volume rendering of the X-ray fluorescence distribution maps of different elements gave unique insights into the morphology and composition of the 17^{th} century paint. The morphology of single pigment particles can be inspected, such as the iron-containing platelets, which are not interpreted correctly when studied in two dimensions. Additionally, the ptychographic data enabled to visualize components consisting of low Z elements such as quartz particles and aluminosilicates. By correlating the lead distribution from XRF and the low electron density signal from ptychography, a lead-containing organic material was discovered on the canvas side of the sample. Comparison to the collected MA-XRF data and microscale research on additional available paint samples, confirmed the presence of a so far unknown lead-containing 'layer' underneath the ground layer. This layer probably functioned as a preparatory layer on the canvas, replacing the commonly used glue sizing as preparation of the canvas. The function of this layer was probably to provide a more stable condition of the adhesion between the canvas and the paint layers, as contemporary sources mention that glue sizing is not always sufficient if a paint is hung on a damp outside wall (wall connected to the outdoors). This information was crucial for the understanding of the current condition of *The Night Watch*, which includes many so-called lead soap protrusions. The lead ions participating in the formation of these small globules, have probably originated from the lead-containing preparation 'layer'. The three-dimensional nanoscale research was crucial to interpret the macroscale XRF data, while the information from historical sources was again significant to establish the proposed hypothesis of the lead-containing 'layer'.

In **Chapter 5**, microscale X-ray fluorescence tomography was used for the quantification of smalt-containing paint samples. Three paint samples from *The Night Watch* were studied, representing three different areas in the painting that contain smalt. Smalt is a blue pigment consisting of ground glass. The potash glass is colored by cobalt(II)-ions. The cobalt distribution in the 3D rendering of the tomographic μ-XRF data can be used to identify the smalt particles in the paint samples. By segmenting all smalt particles, the median size of the particles could be determined. Larger particles were used by Rembrandt for thick impasto paint. The particle size also has an effect on the color of the pigment, another reason to use differently sized particles in different areas of the painting. Agglomerative hierarchical clustering based on the intensities of elements commonly found as minor elements in the smalt enabled a pooling of the smalt particles based on their chemical fingerprint (element composition). Smalt with different composition could be distinguished within the samples. This variety can point toward the use of multiple types of smalt for one paint, heterogeneity in the cobalt ore, variety arisen during the smalt manufacturing process or *in-situ* degradation leading to inhomogeneous smalt. In one sample there was also a difference in the average particle size, which also points to the use of a mixture of smalt types by Rembrandt. The three-dimensional distribution of other elements enabled quantification of the paint mixtures used by Rembrandt in different areas of the paint. This study shows how SR-μ-XRF tomography can quantitatively inform on 17^{th} century paint mixtures, while also providing information about the creative process of the painter and the materials used.

6.2 Outlook

6.2.1 Model samples and reconstructions

The complexity of oil paintings and the scarce availability of materials to study – especially for invasive and/or destructive techniques – are limiting factors for the study of chemical reactions taking place in oil paintings. It is impossible for the full lifetime of a 17th century painting to be mimicked in the lab. Not only are accelerated ageing conditions not always representative, but a large part of the object's history is also unknown. Even for important paintings such as *The Night Watch*, a lot of information is missing, for example about the history of the conservation treatments and the environmental conditions of the room or building it was located in during its lifetime of almost 400 years.

To clarify reaction steps in degradation pathways, simple model systems are very valuable. As part of this thesis a project was carried out to explore the local conditions necessary for the formation of different lead arsenates in paintings. A simple experiment was designed by adding lead white to As(V) solutions of different pH levels. In this experiment, in only a few weeks lead arsenates formed in the solution, where schultenite ($PbHAsO_4$) had formed in acidic conditions and mimetite had formed ($Pb_5(AsO_4)_3Cl$) in alkalic conditions. Another set of experiments was performed by artificially light-ageing model systems containing realgar pigment. Also there, the formation of degradation products (pararealgar and arsenolite) could be followed over time, and the formation was again complete in only a few weeks. Following these reactions in real-time will expand the knowledge on the influence of the local conditions on the kinetics of these reactions.

6.2.2 Synchrotron-based research

The majority of the work presented in this thesis was performed at synchrotron radiation facilities. These facilities are very suited for X-ray imaging of paint samples due to the X-ray beam's high spectral brightness and small source size. To obtain measuring time (so-called beam time) at these facilities it is necessary to write a research proposal, which is reviewed by a committee and a selection of the best proposals is granted beam time. The beam time is then scheduled a few months later. This process is very time consuming, and proposals from researchers working on historical materials are often in direct competition with one another. Moreover, some researchers only have a few samples to study.

To increase the efficiency of this type of studies, a block allocation group (BAG) proposal for historical materials was proposed at beamline ID13 and ID22 at the ESRF (Grenoble, France).[1] After the recent upgrade of the ESRF to an extremely brilliant source (EBS)[2], measurements are very fast and if mounted properly, samples can be easily measured in series. Some of the data shown in Chapters 3 and 4 were acquired during beam time accessed through this BAG, and it has proven to be a fruitful collaboration between universities and institutes. Because the participants of the beam time, led by the responsible scientists, learn on-the-go and can help each other in the data acquisition and processing, some of the workload of the beam line scientist is decreased. Additionally, workflows for data processing are also developed to streamline the research process. This type of collaborations should be nourished and expanded to make efficient use of the capabilities of the newest generation of synchrotrons.

Faster measurements also create more possibilities for following (degradation) reactions in paint systems *in-situ*. A BAG proposal at beamline P06 (PETRAIII, DESY, Hamburg, Germany) was allocated to study this type of reaction in both two and three dimensions. This will not only allow the reactions to be followed in real-time, but also with spatial information on the reactions. Within this BAG, partners are working together not only based on a resemblance in the studied materials, but also in the used set-ups and type of experiments. Measuring cells that were designed to study heterogenous catalysts[3] will now be used to study the interaction of pigments, in real time, with gasses and light exposure. By expanding this type of measurements to more complex model systems, the chemical reactions taking place in paint systems can be studied even more closely. This type of experiments can also be used to follow the chemical interactions between the paint material and conservation treatments, both to understand what might have happened to paintings in the past, as well as to make informed decisions on future treatments.

6.2.3 Processing large data sets

With the implementation of more analytical techniques in the field of heritage science, more types of data are generated. Additionally, technical developments are enabling faster measurements, allowing researchers to measure larger areas of paintings or paint samples, or more samples. With this growth in both the types as well as the amount of data, it becomes more challenging for researchers to process all data correctly, without missing any important information. Luckily, with these developments also workflows for data processing are under development, and with increased computing capabilities many workflows can now be executed on personal computers and laptops.

In general, statistical methods such as principal component analysis (PCA) followed by K-means or hierarchical tree clustering, but also t-SNE algorithms[4,5] are a great way to reduce the large data sets collected in 2D or 3D scans, and can help the researcher to find interesting areas in the painting or sample. Although these techniques are more commonly used in cultural heritage (CH) research papers over the last years, there are still many studies that lack this type of data interpretation. Using multivariate data analysis can also often resolve biased data interpretation based on prior knowledge.

6.2.4 Machine learning and artificial intelligence

The next step in processing the data collected in research on paintings will be to combine results from different analytical techniques, and/or techniques on different length scales. Machine learning (ML) and artificial intelligence (AI) can play a role in this. As part of this PhD thesis, a neural network (NN) project was initiated to look into the viability of the predication of MA-XRD based on MA-XRF data. The availability of commercial MA-XRF scanners has led to quite a widespread presence of this type of devices in museums and research institutes, while only very few institutes have access to a MA-XRD scanner. The molecule-specific results of MA-XRD make it possible to identify degradation products, which is not the case for MA-XRF. The NN in the project was trained on both MA-XRD and MA-XRF data. The NN was then fed new MA-XRF data and was asked to categorize the pixel. The categorization in 16 pigment and degradation classes was unsuccessful, therefore four categories were chosen: 'Original', 'Risk', 'Degraded' or 'Other'. This way, based on the MA-XRF, degraded or at-risk of degradation areas in the painting could be identified. Double hidden layer NNs trained on raw MA-XRF data worked best, with an accuracy of 77 % and recognizing 88 % of all degraded pixels. The tests were only performed on the dataset of one painting, and the next step would be to test the NN on similar paintings (same artist, material, period and support). Because it is expected that the results on a new painting would be worse, it is advised to add an additional type of data in the training of the NN, such as high-resolution photographs.

This type of model would not only help conservators and scientists to identify at-risk or degraded areas in paintings, but it could also assist in the selection of sampling locations. Ideally, the information on paint samples from the painting would then also be implemented in the training of the model to improve accuracy, and in the end the aim would also be that less sample taking is necessary. The challenge in the successful development of such a model does not only lie in providing adequate training data, but also in the different length scales of the data. A recent study shows how the difference in resolution of MA-XRD, MA-XRF and RIS data can be partly resolved with a ML approach.[6]

Next to the prediction of results based on limited data, ML and AI can also play a role in the improvement of collected data. A recent study[7], presents a deep learning algorithm that improves the accuracy of quantifying fluorescence line intensities as well as limits the effects of common artefacts for MA-XRF scans of paintings. This is especially useful for the improvement of elemental maps of elements with overlapping x-ray peaks such as lead, arsenic and mercury.

ML and AI will play a pivotal role in all fields of scientific research in the coming years. The field of heritage science will be no exception. The limited availability and accessibility of scientific equipment at many museums and heritage institutions emphasizes the importance to get the most out of the data available. To improve the possibilities to implement ML and AI across the field, it is important to collect and store data following the FAIR data principle. FAIR is an abbreviation for Findable, Accessible, Interoperable and Reusable. Registration of exhaustive meta data is very important to be able to compare datasets. FAIR data storage will also help in successful data fusion of different types of data. Ultimately, multivariate analysis or ML and AI methods can be used on the whole bulk of different data, which is expected to result in unforeseen correlations between data types. This will help to determine which type of data is crucial for specific research questions but is also expected to play an important role in authenticity questions. It is of great importance that trained scientists are constantly involved, to make sure that the provided data is interpreted correctly.

6.2.5 Historical sources and expert knowledge

Historical sources are very valuable in cultural heritage research. There are specific sources that 17th century painters would use to learn what materials to use and to learn about specific paintings-related methods such as preparation of the canvas.[8–10] Other historical sources mentioning pigment manufacturing, pigment trading routes, and even shop lists of pigments sellers or apothecaries are invaluable to understand what materials were available in the 17th century in what places. In Chapters 3, 4, and 5, historical sources were important factors in (dis)proving hypotheses brought up by the analytical research. Research into historical sources is an expertise of its own, as these sources are often difficult to find, translate and read. Working together with specialists such as (technical) art historians and conservators is key.

Next to written information, a lot of information can be gained from talking to experts with hands-on experience and specialized skills. Conservators spent many hours working on paintings at a very close distance, during which they gain unique knowledge on the materials of oil paint. Some of their expert knowledge is difficult to grasp into writing. When taking a microscopic paint sample with a scalpel, some paint is easier to cut through than other material, and this type of feeling is difficult to describe, though it can give a lot of information about the condition of the paint. Ideally, this knowledge from the conservator would be captured as much as possible through interviews and written reports. When thinking of a large ML or AI model to feed scientific data into, this information should also be added. Ultimately, this could result in a model that can assist (junior) conservators and scientists involved in the next conservation treatment of a Rembrandt painting, based on the input and knowledge gained from *Operation Night Watch* and other Rembrandt related research. The model could highlight areas in the painting with a possibly at-risk condition or suggest areas where a sample could be taken to investigate the paint layers further. The goal would be to act as an assistant to the conservators and scientists, as well as a way to maintain as much knowledge as possible for future generations.

6.3 References

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