Exploring the chemical interactions of lead(II) oxide and linseed oil in historical and model paint systems using laboratory and safe synchrotron radiation analysis

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Chapter 6 Conclusion and Outlook

6.1 Conclusion

In this chapter we offer the conclusion of the studies in a wider context, and the implications for conservators, together with future perspectives.

In **Chapter 2**, the presence and spatial distribution of lead(II) formate (LF), detected for the first time in historical paintings, notably in *The Night Watch* were studied. SR-μ-XRPD analyses showed similarities in the formation and spatial distribution of LF in *The Night Watch* and the model samples. Optical microscopy of simplified lead(II) oxide (PbO) and oil model systems demonstrated that LF crystals form rapidly within the first days of curing and remain stable for at least three years under room temperature conditions. Mapping of thin cross-sections of these model systems further suggested that LF distribution is influenced by factors such as paint thickness, PbO concentration, and the presence of pigments. Besides LF, model systems showed the formation of lead(II) formate hydroxide (LFH) as a more alkaline form around PbO particles. Additionally, plumbonacrite (PN) - a rare lead carbonate only stable in alkaline conditions - was found colocalized with LF in both *The Night Watch* and model systems. These findings indicate that LF formed in *The Night Watch* from a reaction between Pb(II) ions from an alkaline lead source, such as PbO-based drier, and formic acid coming from the linseed oil (LO) oxidation reaction. Historical treatises, including the one by Turquet De Mayerne (1633), indicated that artists prepared a cooked PbO-oil mixture (*huile de litharge*) to modify paint properties. The predominant presence of LF in light-toned, lead-white-rich areas of *The Night Watch* suggests that Rembrandt may have used such a saponified lead-based medium to enhance the thickness and handling properties of his *impastos*. Another potential source of LF in *The Night Watch* may come from an 18th century re-varnishing treatment using an oil-rich varnish, which may have emitted formic acid. Additionally, the Pb(II) ions necessary for LF formation may have originated from a lead-containing pigment rather than exclusively from a PbO-based drier. To explore this hypothesis further, experiments should be conducted by applying an oil-rich varnish, prepared according to historical recipes, onto an aged lead-pigment-based model system. The lead and oil interface could then be analysed using SR-μ-XRPD on transversal thin sections to determine potential mechanisms of LF formation. SR-μ-XRPD analyses of both historical and model samples conducted within this study demonstrated that under prolonged exposure to high-intensity X-ray radiation (higher flux, dwell time, and scan repetitions), LF can undergo reduction to metallic lead (Pb(0)). This result motivated the study on X-ray-induced alteration assessment in Chapter 5.

In **Chapter 3,** the ground layer of *Mona Lisa* painting was studied. SEM-EDS analyses of the micro-fragment revealed presence of Pb as the main component of the ground layer. Additionally, the SR-HR-XRPD analyses revealed presence of hydrocerussite (HCer) and cerussite (Cer) as a part of the lead white pigment. Unexpectedly, these analyses revealed peaks attributed to PN for the first time in an Italian Renaissance painting. As revealed in the previous chapter, PN is correlated to an alkaline Pb source, such as leaded oil. Additionally, μ-FTIR analyses showed peaks attributed to lead carbonates specific to lead white (LW) and of a strongly saponified oil. SR-μ-XRPD and SR-μ-FTIR analyses of *The Last Supper* showed presence of PbO and correlated lead-based products (such as PN, HCer and first-time detected shannonite, SH) colocalized in an intermediate layer between the ground and coloured paint, sometimes dispersing as small particles throughout both. Finally, SR-μ-XRPD analyses of PbO and oil model systems revealed similar finds: PbO particles were found surrounded with SH, PN an nHCer. Together, these results indicate that Leonardo might have prepared the ground layer of *Mona Lisa* and the intermediate (*imprimatura*) layer of *The Last Supper* with a highly saponified lead-rich oil. Furthermore, a thorough review of Leonardo's historical treatises indicated that he was indeed familiar with the use of litharge mentioned as *letargirio di pionbo* in Codice Arundel (1480 and 1518), and that it was most likely a part of his painting palette.

Chapter 4 explores the early chemical formation pathway and detection of unusual lead carbonate and carboxylate-based compounds by investigating leaded oil model systems, with samples mimicking both well and poorly ground and mixed PbO in oil. Our experimental results indicate that lead carboxylates (LF and LFH) and lead carbonates (SH, PN and nHCer) can all originate from the leaded oil. Additionally, crystalline LF shows high mobility over the paint film during the first days of oil curing, resulting in the heterogeneous distribution over the paint film. LFH and various lead carbonate-containing products form and remain more concentrated in the PbO globule areas. Our results show that the distribution of LF and LFH depends on the levels of alkalinity in the paint film, while the distribution of lead carbonates depends on both alkalinity and CO_2 levels. Beyond the rapid physico-chemical evolution of the leaded oil system - resulting in the heterogeneous distribution of compounds - we observed that the choice of analytical technique impacts the detection of these lead-based products. By relating our model system findings to historical examples, we addressed the rare detection and heterogeneous distribution of these compounds in existing literature. The combination of our experimental results with a review of previous studies enabled us to hypothesize potential main factors impacting its heterogeneous distribution which contributes to their unsystematic detection.

In **Chapter 5**, we assessed the synchrotron X-ray radiation alteration in mock-up paints relevant for safer analyses of historical paint systems. *In-situ* SR-μ-XRPD point analyses showed that upon exposure to high flux (HF) conditions, HCer peaks decreased and broadened, indicating amorphization and loss of crystallinity, while new compounds - Cer and SH - formed under X-ray exposure. Additionally, at both HF and low flux (LF) Pb(II) ions were reduced to Pb(0). *Ex-situ* MALDI-MSI and μ-FTIR analyses showed a difference in molecular composition across non-irradiated and irradiated areas. More precisely, μ-FTIR integrated intensity maps and average spectra showed molecular alterations of LO binder indicative of ester bond homolytic cleavage, formation of fatty acids, their homolytic cleavage into shorter-chain hydrocarbons and decarboxylation which releases CO_2. CO_2 might also come from lead soaps decarboxylation. Lead soaps decompose under intense X-ray exposure, while lead carbonates form, most likely through Pb(II) from lead soaps reaction with CO_2 from the atmosphere or from the decarboxylation reactions. This study shows that the extent of alteration may be influenced by both external (flux, dwell time, and the number of scans) and internal factors (binder/pigment composition and sample age). By testing different X-ray conditions, we defined the most optimal ones - 1 scan, 0.01 s, LF - that offer sufficient data quality while reducing risk of radiation alteration at ID13, ESRF. Experiments on samples of different ages showed that older samples are more resistant to X-ray induced alterations, potentially due to higher level of cross-linking and stronger film formation. Additionally, our results highlight that structural and molecular modifications may occur without visible changes. Unlike visual alterations, molecular changes are irreversible and can lead to misinterpretations in future analyses. Therefore, proper assessment of the modification of the model systems representative of historical systems is crucial when conducting synchrotron experiments.

6.2 Main reflections of the thesis and outlook

The primary objective of this thesis was to investigate the short- and long-term chemical interactions between the PbO drier and oil binder, as well as their associated reaction products, in both historical and model paints.

6.2.1 Complementary macro- and micro-scale analysis of historical and model paint systems

As mentioned in section 1.5, macro-scale analytical techniques have limited ability to resolve the full stratigraphy of complex, multi-layered historical paint systems. To overcome this limitation, our approach focused on micro-scale chemical characterization of historical paint fragments, combining synchrotron- and laboratory-based techniques. This multi-analytical, micro-scale approach enabled the identification and spatial mapping of PbO and oil reaction products within historical paintings. However, such localized analyses based on paint fragments cannot fully capture the chemical composition of the entire painting, which may be influenced by other potential local material additions by the artist, heterogeneous degradation, and localized conservation treatments. Moreover, the high complexity and heterogeneity of lead products in paint layers, along with their low concentrations make their unambiguous detection particularly challenging. Additionally, centuries-old historical fragments offer limited insight into the early stage reactions and kinetics.

To overcome these challenges, simplified model systems composed of PbO and oil were prepared and analysed, both naturally and artificially aged. These controlled systems offered valuable insights into the initial chemical pathways and kinetics of reactions between PbO and oil. However, such model systems cannot fully replicate the complexity of historical paintings, which are influenced by a range of factors, such as artistic materials and techniques, environmental conditions, and conservation treatment history. For instance, the hypothesis that LF formed in the surface layers of *The Night Watch* as a consequence of oil-rich re-varnishing conservation treatment remains open (discussed in Chapter 2). This hypothesis requires further investigation using model systems that closely mimic the paint stratigraphy and conservation treatment.

Therefore, when using simplified and controlled systems to study the complex chemistry of oil paintings, it is essential to recreate and consider the many different factors in model systems that may influence chemical reaction pathways. Moving forward, the development of advanced tools - potentially incorporating artificial intelligence - could enable researchers to translate the information obtained from micro-scale analyses to the macro-scale. These tools may enable the prediction of reaction patterns across other, similar areas of the painting, based on micro-scale chemical data.

6.2.2 *Synchrotron radiation analyses and radiation alteration*

Our model systems showed that PbO and oil reaction products can form rapidly and may transform to other products. In early stages, these products show high mobility, leading to heterogeneous distribution within the paint system. Combined with their typically low concentrations and complex matrices in historical samples, these characteristics make their detection particularly challenging. To reliably detect the PbO and oil products, highly sensitive and selective synchrotron-based analytical techniques are recommended. However, as shown in Chapter 5, synchrotron radiation poses a risk of radiation-induced alterations, which alter the sample composition and data. Given that the preservation of the object is the final goal of scientific analyses, preserving the integrity of even the smallest micro-samples during the experiments is equally important. These samples should be carefully preserved also because the future advancements in analytical techniques may reveal information that are currently inaccessible. To assess the extent of radiation alteration and understand the chemical reactions at stake during sample exposure to X-rays, we analysed mock-up samples representative of historical systems using a multi-analytical approach. While these mock-up samples provided valuable insights into radiation-induced changes, they cannot fully replicate the aged, multi-layered, and often varnished nature of historical paint systems, which may respond differently to X-ray exposure. It is practically impossible to replicate the exact complexity of historical paint fragments and predict their reactions under the X-ray beam. However, we can tailor our synchrotron experiments more carefully and take certain precautions beforehand:

1. Begin with low-dose X-ray conditions to minimise the risk of radiation alteration of the sample and data.

2. Use complementary non-irradiating techniques before and after X-ray exposure to distinguish between original compounds and radiation-induced products.

3. Monitor irradiated samples long-term, as radiation-induced changes can be delayed. New reactive species formed during exposure may migrate and interact with unirradiated areas over time, leading to the formation of secondary products that appear well after initial analysis.

These practices help minimise the risk of radiation-induced changes to the samples and data, and avoid potential data misinterpretation.

Looking ahead, it would be highly beneficial to conduct kinetic studies using synchrotron X-rays, given their advanced analytical capabilities. However, such studies require prolonged exposure of samples to the analytical beam, which - particularly in the case of synchrotron radiation - may lead to significant radiation-induced alterations. To prevent these effects, further assessment of radiation alteration on mock-up samples is needed, under different X-ray conditions and for extended periods. In the meantime, laboratory-based techniques offer a less invasive alternative for kinetic measurements and can be complemented by synchrotron-based analyses conducted under low-dose conditions.

Furthermore, new developments are ongoing in the field to minimise radiation-induced sample alteration through the use of digital modelling. The impact of radiation can be predicted in advance by employing numerical modelling using synthetic spectral data and optimal experimental conditions. This approach enables a balance between maximizing spectral information and minimising radiation exposure, which additionally prevents radiation alteration and at the same time supports more sustainable experimental practices.

6.2.3 From fundamental to applied knowledge

This thesis offers a deeper understanding of artists' intentions by investigating their materials and techniques through scientific analyses of both historical and model paint fragments, complemented by a bibliographic review of historical treatises. This interdisciplinary approach sheds light on the chemical and physical transformations that artistic materials undergo over time, as well as on the formation of products resulting from these changes.

At the moment, the scientific findings presented in this study do not yet translate into direct practical measures for conservation practice. This is primarily because the investigated lead-based reaction products are rare and their impact on the long-term stability of paintings remains underexplored. For instance, in Chapter 4, we demonstrated that a model system containing PbO formed lead carbonates upon exposure to atmospheric CO_2. One might hypothesize that a similar reaction could occur when a paint surface is exposed to air during varnish removal treatments. However, translating such chemical insights into practical conservation strategies is not linear and straightforward yet, especially as the chemical composition of the model systems is significantly simplified compared to that of historical paintings. Therefore, exploration of different types of model systems illustrating different aspects combined with further interdisciplinary collaboration between scientists and conservators is recommended. A critical next step involves evaluating with conservators whether these rare lead-based compounds have beneficial, detrimental, or neutral effects on the long-term stability, appearance, and integrity of the paintings. Only through such careful assessments can conservation treatments be tailored.

In addition, the protocols developed in this thesis for assessing radiation-induced alterations offer the scientific and conservation communities a safer and more predictive approach for conducting synchrotron-based analyses on sensitive historical materials.