Binding medium, pigments and metal soaps characterised and localised in paint cross-sections

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Paintings are complex systems that continuously undergo chemical and physical alterations. The analytical studies of paintings reported in this thesis are performed on the microscopic and molecular level with the ultimate aim to utilise the acquired knowledge of the alteration processes to improve display and storage conditions, suggest suitable restoration treatments and address art historical issues.

The microscopic and molecular studies are carried out on tiny paint samples derived from paintings. Paint samples are embedded in resin and polished until a flat cross-section of the layer system, the so-called paint cross-section, is visible at the surface. By preserving the layer structure of the sample, the distribution of pigment, binding medium components and their aging and degradation products can be charted. The analysis of paint cross-sections with spatially resolving analytical imaging techniques facilitates the identification and localisation of the molecular and elemental composition in the paint sample.

Different non-destructive analytical imaging techniques applied to the same paint cross-section result in a combined set of data that gives a more complete impression of the chemical composition of the paint sample. The following techniques have been applied: light microscopy, imaging Fourier Transform Infrared spectroscopy (imaging-FTIR), scanning electron microscopy combined with energy dispersive X-ray analysis (SEM/EDX) and imaging static secondary ion mass spectrometry (SIMS).

SIMS applied to paint cross-sections from Old Master paintings is a relatively novel approach. SIMS is introduced as an analytical technique for the examination of paint cross-sections in chapter 2. The paint cross-section discussed in this chapter was taken from the blue robe of Maria in the panel painting The Descent from the Cross (Museo del Prado, Madrid) of the Early Netherlandish artist Rogier van der Weyden (1399/1400-1464). This 15th-century panel painting is in a very good condition, which makes the paint cross-section a suitable example of pigments and binding media in oil paintings. The identification of the pigments in the paint cross-section is based on the elemental composition. The shape and position of the sodium and aluminium in the SIMS image corresponds exactly with form and position of the ultramarine particles and the copper SIMS image matches the azurite particles observed by the light microscopy. The elemental composition and distribution is in agreement with the SEM/EDX results. The molecular information obtained with SIMS is representative for oleaginous binding media. The interpretation of the ion

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peaks characteristic for binding medium constituents in the SIMS spectra is supported by spectral data from reference materials. SIMS fragment ions characteristic for drying oil are found in the upper three paint layers while the ratio of palmitic and stearic acid derived from the negative ion distribution pattern in each of the upper three paint layers is indicative of linseed oil. SIMS also detects lead soaps in the paint layers, which is indicative for a mature aged oil paint. The presence of lead soaps in these paint layers is confirmed by the results of imaging FTIR. SIMS is considered to be a very suitable analytical tool for the identification and localisation of the binding medium and pigment present in paint cross-sections.

The following chapters (3, 4 and 5) present different aspects of the paint (binding medium, pigment and their interaction products) studied with the various analytical imaging techniques mentioned above.

SIMS is one of the few non-destructive techniques that yields detailed spatially resolved molecular information on the micrometer scale. SIMS is therefore suitable for the study of binding medium in paint cross-sections. The scope of this technique for the localisation and identification of the oil binding medium is discussed in chapter 3 which is divided in three separate sections: the interpretation of the SIMS spectra, the localisation of oil paint constituents, and enhancement of the yield of organic ion.

A natural and accelerated aged linseed oil paint reconstruction is analysed as model system by SIMS, DTMS and GC/MS as three different mass spectrometric techniques. Comparison of these data gives a good impression of the value of the molecular information on the oil medium obtained with SIMS. SIMS provides important combined information on the organic and inorganic components of the upper atomic layers of the analysed surface of the paint film. Characteristic peaks representative for the fatty acids as important oil paint constituents are detected as negative ions. Positive ion spectra provide detailed chemical information on the condition of the oil paint by distinguishing the speciation of the fatty acids in free, ester-bound or metal carboxylate form. SIMS does not produce significant yields of diacids and little relevant information concerning the polymeric network. GC/MS results on the other hand show that diacids are dominantly present and DTMS is more informative about polymeric network. Despite these limitations, I conclude that SIMS is a valid and important analytical method for the study the oil binding medium of paint samples.

The localisation of characteristic peak representative for fatty acids and their ratio in paint cross-section in the topic in the second section of chapter 3. SIMS studies of pure fatty acids mixed in a chalk matrix show that the response of the negative ions from the various fatty acids tested is identical under the SIMS ionisation conditions. Hence, the determination of the P/S ratio by SIMS is a valid method for
the identification of the type of oil in a paint layer. P/S ratios were determined in individual layers from 15th- to 19th-century paintings using paint cross-sections. Studies on non-fully dried multi-layered test oil paint systems of linseed and poppy oil by SIMS demonstrate P/S ratios that suggest a rapid exchange of oil triacylglycerols between the layers, which has relevance for the interpretation of paint systems made with the wet-in-wet technique. Positive ion SIMS mass spectral data presents information on the distribution of the free, ester bound or metal carboxylate the fatty acids in the paint layers.

In the last section of chapter 3 data are presented on the surface of a cross-section that is coated with a 20Å thick gold layer to improve the yield of secondary ions from organic fractions in the paint. The improvement is shown using a chalk tablet with 1% stearic acid of which one half of the surface is gold coated. A comparative study of a gold-coated native and aged surface of a linseed oil paint reconstruction further demonstrates the enhancement of the organic ion yields on this sample relevant for painting studies. The yield of oil paint derived negative ions increases by a factor of 3 whereas the yield of positive ions increases by a factor of 2 to 4. Gold coating improves the ionisation process of the fatty acids and does not influence their fragmentation. The gold coating method is applied to one paint cross-section presented in chapter 5 illustrating the improved quality of the data on the distribution of the different organic constituents of the oil medium (mono- and as well as dicarboxylic acids) in the paint sample.

Chapter 4 illustrates the different imaging analytical techniques applied to a paint cross-section complement each other in the description of pigment degradation phenomena. The light induced blackening of the traditional red pigment vermilion (mercury sulphide) is a century old problem. The blackening of vermilion is a phenomenon on the surface of paintings, which is illustrated in the paint cross-section as degraded pigment on top of intact vermilion. Detailed light microscopic images of a paint cross-section originating from a painting by Rubens (17th century) reveal a black and a white coloured reaction product. The position of the black and white products in the paint cross-section and the presence of partially degraded vermilion suggest that the white coloured products are formed after the black reaction product. SEM/EDX as well as SIMS data visualise the elementary and molecular composition and their distribution in the paint sample. Both techniques detect a high relative concentration of chloride in the degraded vermilion, while SIMS is sensitive enough to map chlorides in the intact vermilion. In contrast to SEM/EDX, SIMS can detect inorganic molecules and is able to identify the white product as mercuric chloride (HgCl₂). The distribution of atomic and molecular species in the paint cross-section leads to the formulation of a new hypothesis on the photo-degradation mechanism of
vermilion. We propose that traces of chloride catalyse a light-induced electrochemical reaction that converts red vermilion into a black product. The current interpretation that the black product is metacinnabar form of HgS is not supported by our investigation. The black product is proposed to be composed of residual vermilion with nanodroplets of metallic mercury that absorb the light. We observe that a relatively high amount of chloride is accumulating in the black product, which reacts with the mercury to white mercury chlorides. This mercury complex is described in paintings for the first time. The blackening of vermilion is an irreversible process, in which chlorides play an important role. For preventive conservation of vermilion containing works of art, exposure to chloride-containing compounds should be prevented.

Chapter 5 illustrates that binding medium and pigment cannot be seen as separated entities in paints because numerous paintings from the 15th to the 20th century are affected by metal soap aggregate formation. Ten paint cross-section that contain paints with lead or zinc soap aggregates were selected for investigation with the different imaging analytical techniques. Lead and zinc soap aggregates have a negative effect on the stability of the painting and as they can protrude through the surface they affect the appearance of the painting. Metal soap is formed in a chemical reaction between a fatty acid, derived from the oil medium, and a metal ion originating from pigment or drier. Metal soaps are normally formed in oil paintings, but many examples are found with an excess of metal soaps, which can lead to aggregation. Imaging analytical studies on the selected paint cross-sections derived from paintings by e.g. Rembrandt van Rijn (17th century) or Vincent van Gogh (19th century), have shown that in some cases the pigment completely reacts away. The reactive fatty acids are released during ageing of the oil, but in certain cases these fatty acids presumably cannot be directly incorporated in the oil network but migrate to the pigment surface. The reactive fatty acids can derive from the saponified paint layer or from other paint layers in the multi-layered paint system. Formation of mineralised matter is observed inside the aggregates, identified as lead carbonate in lead soaps or zinc carbonate in zinc soaps. In some cases, tiny orange minium (lead plumbate) crystals are seen on the inside of the edge of the lead soap aggregates. Metal soap aggregate formation is an irreversible process, the imaging studies however lead to better insight into some of the parameters which play a significant role in the formation of an excess of metal soap in paintings. Moisture and high temperature are two of these factors, which not only promote the hydrolysis during ageing of the oil paint, but also increase the reactivity of fatty acid and pigment. Reduction of the mobilisation of fatty acids in paintings by e.g. avoiding moisture and heat during restoration treatments and the optimizing storage conditions might reduce the risk of metal soap aggregation formation.