Color changes and chemical reactivity in seventeenth-century oil paintings
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Improving the Surface Quality of Paint Cross-sections for Analytical Imaging Studies with SR-FTIR and Static-SIMS

**ABSTRACT** – The importance of high-quality surface preparation for analytical imaging studies of paint cross-sections is illustrated in this chapter. A systematic dry polishing method was developed based on mechanical preparation with the sample fixed in a polishing holder. Using this method, the surface of existing paint cross-sections was re-polished and re-measured resulting in higher quality analytical data. A thin proteinaceous isolation layer in the flesh paint of an eighteenth-century German polychrome sculpture by Ignaz Günther was studied using specular reflection Fourier transform infrared (SR-FTIR) imaging. SR-FTIR also distinguished the different resinous, proteinaceous and carbohydrate components in the varnish of a Van Gogh painting. In the last example, a cross-section from a painting by Vermeer was examined using static-secondary ion mass spectrometry (static-SIMS) imaging. Here, the higher surface quality led to better mass and spatial resolution.

**INTRODUCTION**

Historical paintings and polychromes often show a complex multi-layer build-up with heterogeneous mixtures of organic and inorganic compounds, specifically binding media, pigments and additives. Embedded paint cross-sections are the preferred method of revealing their stratigraphy. The same cross-section can be used for multiple investigations using different non-destructive analytical microscopic imaging techniques. Commonly used imaging techniques are light microscopy (LM) and scanning electron microscopy in combination with energy dispersive X-ray analysis (SEM-EDX). During the MOLART and De Mayerne MOLMAP projects, novel chemical imaging techniques, specular reflection Fourier transform infrared (SR-FTIR) imaging and secondary ion mass spectrometry (SIMS) imaging, used successfully for the analysis of embedded paint cross-sections, in particular the organic components, were developed [Heeren and Boon 1999, Weerd et al. 2002a, Keune and Boon 2004]. SR-FTIR imaging provides information on the distribution of chemical functional groups in a paint cross-section, such as amide groups that are indicative of proteins or the carboxylate group in lead soaps with a spatial resolution of 6 to 7 μm. A full infrared spectrum is collected for each pixel. Results can be displayed as two-dimensional images of a selected functional group to show its intensity distribution on the surface of the cross-section. In a SIMS

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1 MOLART (1995-2002) brought different disciplines together and created a research platform for the study of the material science aspects of paintings in historical context. It was funded by the Netherlands Organization of Scientific Research (NWO). The De Mayerne program continued this effort for the period 2002-2006. In the MOLMAP project as part of the De Mayerne program, the molecular mapping of paint cross-sections was further explored.
experiment, a primary ion beam rasters over the cross-section surface and generates organic and inorganic secondary ions from the sample, negative ions like fatty acids or positive ions such as lead soaps. Thus, spatially resolved mass information of components present in the paint layer is obtained and can be plotted as two-dimensional images that demonstrate the intensity distribution of a mass peak of interest on the surface of a cross-section with a spatial resolution up to 1 μm. The different imaging techniques are complementary and their combined use provides detailed information on the chemical composition and spatial distribution of both the organic and inorganic substances present in the paint. Knowledge of the composition of individual layers is obtained without the need to separate the layers prior to analysis.

The advanced microscopic techniques, however, require a high surface quality to obtain any results. The surface needs to be exactly in plane and any chemical modification of the layers or smearing of the embedding resin or sample over the surface must be avoided. The polishing step is essential to sample preparation. It is complicated by differences in hardness within the paint, the coarseness of the pigment particles and the overall brittleness of the paint. The existing polishing methods were found to be insufficient and were in need of serious re-evaluation to fulfill the high requirements of surface-sensitive analytical techniques. A recent review of the literature related to making paint cross-sections from easel paintings was written by Khandekar [Khandekar 2003]. Mechanical preparation is the most common method of preparing historic paint samples for microscopic examination. The sample is first embedded in a synthetic resin and ground and polished. Abrasive particles are used in successively finer steps to remove material from the surface until the required result is reached. Microtoming is another method of preparing cross-sections, as well as thin sections. A thin layer is removed from the mounted cross-section with a glass or diamond knife, but the technique is less suitable for the preparation of historic paint samples, since particles or part of the sample easily fall from these brittle paints during the cutting process. However, microtoming is very efficient and successful when preparing more plastic samples from paint reconstructions or from modern paintings. Instead, Van der Weerd developed a double polishing method, where the sample is mounted in potassium bromide (KBr), an infrared transparent medium, for transmission FTIR imaging studies [Van der Weerd 2002b]. Recently, more advanced (and also more costly) preparation techniques are being explored. Ion milling (CP system) [Boon and Asahina 2006] and Dual Beam/Focused Ion Beam (FIB) tools [Lins et al. 2002] were specifically developed for SEM and TEM applications and provide better morphology and particle definition. However, the suitability of these techniques for organic analyses must be examined. These systems use beams of argon or gallium ions for site-specific milling of cross-sections that may damage/destroy organic compounds on the surface.

In this study, we developed a systematic method to dry polish paint cross-sections based on mechanical preparation. This revised method has been successfully applied and has led to significantly better analytical results. For SR-FTIR, the results were improved because the new method increases surface reflectivity. In a static-SIMS

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2 Although with care some of the disadvantages can be reduced [Kirby 1977; Derrick et al. 1999].
experiment, the higher surface quality provides better mass and spatial resolution. The polishing method will be described in the next section of this chapter. Subsequently, the improvement in analytical image data quality will be illustrated in three case studies.

The importance of a high surface quality for the surface-sensitive imaging techniques also has consequences for the sequence of analysis, when various techniques are applied to the same cross-section and the resulting images are combined and overlaid to obtain complementary information on the paint composition. Therefore, we developed the following protocol in our laboratory. First, we performed specular reflection FTIR measurements, since this technique is completely non-destructive. Afterward, SIMS and finally SEM-EDX analysis were performed. High vacuum SEM-EDX systems require a carbon coating; the removal of this coating modifies the surface. In addition, the electron beam may sometimes burn small holes in the surface during EDX spot analysis or leave a black square after EDX mapping, which negatively influences the FTIR and SIMS measurements.

MECHANICAL DRY POLISHING METHOD

In this section, different factors that are important for the polishing process of paint cross-sections and the resulting surface finish will be considered.

WET POLISHING VERSUS DRY POLISHING

The abrasion fluid has a cooling role and a flushing role: it prevents the specimen from overheating and removes the loose material. Water, as well as organic solvents such as kerosene, alcohol or oils, are used as abrasion fluids. When paint cross-sections of historic paintings and polychrome are polished, the disadvantages of using abrasion fluid are numerous in our experience. First, soluble paint constituents may be leached out by the abrasion fluid, for example a chalk ground by water or fatty acids by spirit solvents. Second, the blanching of old varnish layers was observed. Third, softer materials erode and hollow out the cross-section. Fourth, weakly bound particles such as coarse minerals may easily be picked up by the abrasive fluid. Fifth, the uneven swelling of the layers during wet polishing causes height differences in the surface. These drawbacks make wet polishing absolutely unsuitable for our purposes. Dry polishing is the only option, and therefore, it is necessary to identify a method that reduces friction and removes loose material.

ABRASIVES

Most commercially available polishing materials are developed for wet polishing. We tested a couple of different brands without the use of an abrasion fluid, but the results were far from satisfactory. Adhesion of the abrasive to its support turned out to be weak and abrasives accumulated on the surface. Diamond paper and powder were also tested by us, but we have to conclude that a diamond abrasive is too hard for paints because it ruins the entire sample. The hardness of silicon carbide (SiC) and aluminum oxide
Improving the surface quality of paint cross-sections for analytical imaging techniques

(Al₂O₃) are similar. Both of the materials can cut glass particles, although SiC is more porous and breaks out more easily causing scratches and pull-outs on the surface. It seems that Micro-Mesh® sheets³, developed for dry polishing of airplane windows, are the only polishing materials with sufficient adhesion and suitability for dry polishing paint cross-sections. The only drawback is that the particle fineness of the sheets does not go below 1 µm, which is not very high in comparison to wet polishing sheets, which can be as small as 0.1 µm, and abrasive powders, such as aluminum hydroxide (Al(OH)₃), which are about 0.04 µm, at their smallest size.

POLISHING HOLDER

Our goal is to attain a completely focused image with all the components in the same plane. Any unevenness in level of the cross-section surface will show in reflection imaging. When polishing by hand, the pressure exerted on the cross-section is uncontrolled and often too much resulting in rounded and deformed surfaces and deep scratch grooves. Additionally, excessive weight forces harder particles deeper into the paint layer or particles can be rubbed away from the matrix instead of being cut with the abrasive. Higher forces also increase the temperature at the surface because of higher friction, which may cause thermal damage to occur. Therefore, we use polishing holders that were developed in our institute to exert even and minimal pressure on the cross-section (Fig. 1.1). The cross-section block is mounted with wax or small screws and the height is adjustable to one micrometer. The holder can also rotate on the polishing machine for the first wet steps. The weight of the holder (c. 400 gram) is enough to effect cutting by just moving the holder forward, avoiding extra pressure downwards.

MOUNT DIMENSIONS AND SHAPE

Furthermore, a reduction in the embedding resin surrounding the sample, as well as

³ Micro-Mesh sheets are supplied by Micro-Surface Finishing Products Inc., Wilton, Iowa, USA, see their website http://www.micro-surface.com. Micro-Mesh polishing sheets are made of abrasive crystals on a resilient layer over a cloth back. Silicon carbide is used as abrasive for the grades 1500 through 6000; aluminum oxide is used for the finest grades 8000 and 12000.
a rounded shape of the resin block, are expected to positively affect polishing results. Polishing by hand makes a larger surface area of the cross-section necessary to keep the resin block oriented as straight as possible during polishing. According to Samuels, mounts smaller than one-inch diameter tend to rock excessively during hand abrasion and polishing operations [Samuels 1982]. A large surface area also increases the risk of smearing out mounting resin on the paint sample or picking up loose particles. When using a holder, the sample is fixed and straight, so that the surface area of the resin can be reduced to a minimum, which is another advantage of the holder.

The shape of the cross-section also affects polishing. A square or rectangular shape provides more resistance at the corners, therefore, a round shape is preferred. The so-called Easy Sections (VWficit, England) are unsuitable in this respect, because they have a rectangular shape and the length is three times the width, which gives a very uneven resistance.

TECHNIQUE
For the preliminary stages, we use a Struers polishing machine with flushing water and coarse silica abrasive paper (grades 500 and 1200) to grind away the mounting medium until almost reaching the sample. Then, we change to dry polishing. After exposing the sample, the sample is left in the holder and the height is not adjusted further for the final polishing steps.

For dry polishing, a very short and straight movement in one direction is made (about 1-2 cm) to avoid as much friction, smearing and heating as possible. No extra downward pressure should be exerted during the movement, only forward. The weight of the polishing holder itself supplies a constant and sufficient pressure to the specimen surface. The polishing holder is turned 90 degrees. Two full rounds are usually enough before going to a successively finer abrasive step (Fig. 1.2). In any case, it is recommended to restrict polishing times to prevent surface modification.

CONTAMINATIONS
Loose abrasive particles or other loose particles on the specimen surface can be removed with lens tissue or blown away with nitrogen gas. We have noticed that special lens tissue does not leave scratches on the surface, whereas other papers do. We also recommend using clean polishing sheets as much as the budget allows. Used sheets contaminate the surface when re-used. In addition, they contain many loose particles, which can be picked up by the sample and pressed into the surface of the specimen causing new scratches and pits.

EXPERIMENTAL
SAMPLES
We selected three representative paint cross-sections to show the importance of surface preparation. These cross-sections were submitted to our laboratory for analysis, but
their surface as received was too poor to obtain satisfactory results. The first sample concerns the flesh paint from the polychrome wooden sculpture of Saint Isidor by Franz Ignaz Günther (c.1765, St. Francis Xavier altar, Abbey Church in Rott am Inn, South-Germany). The sample is taken from Isidor’s face. Interestingly, it contains a thin intermediate organic layer between superimposed calcium carbonate (chalk) and basic lead carbonate (lead white) layers. This sample was studied using SR-FTIR imaging and additional SEM-EDX analysis was performed. The second cross-section comes from the orangey yellow road in Falling Leaves (Les Alyscamps), painted by Vincent van Gogh in the autumn of 1888 in Arles (Kröller Müller Museum Otterlo inv. no. 224, F486, oil on canvas, 73 x 92 cm). The cross-section shows a thick, yellowed (or better browned) varnish on top of a yellow paint layer consisting of lead chromate, barium sulfate (barite) and calcium sulfate (gypsum) in oil. Isolated sample material of the varnish was analyzed using DTMS and single-point transmission FTIR. FTIR imaging was conducted to localize the different components within the cross-section. The third sample is collected from the background of Johannes Vermeer’s painting Diana and her Companions (c.1655, Mauritshuis The Hague inv.no. 406, oil on canvas, 98 x 105 cm). This paint cross-section demonstrates lead carboxylate aggregates in an intermediate lead-tin yellow layer and primarily smalt particles in the top layer. This sample was examined using static SIMS.4

SAMPLE PREPARATION
The samples were already embedded in either polyester or acrylate resin. Their surface quality was improved by applying the dry polishing method described in the previous section. The sample from Saint Isidor was embedded in Technovit 2000 LC mounting resin, which is a one-component methacrylate that polymerizes under visible blue light (Heraeus Kulzer GmbH, Germany). The Van Gogh sample was embedded in Poly-pol PS230 polyester mounting resin with M.E.K.-peroxide harder (Poly-Service, Amsterdam). The Vermeer sample was embedded in an Easy Section (VWFecit, England) also using Poly-pol PS230 polyester mounting resin.

LIGHT MICROSCOPY
Light microscopic studies of the paint cross-sections were performed on a Leica DMRX analytical microscope (Leica, Wetzlar, Germany). A 100W Halogen projection lamp provided normal reflected light in bright field and in dark field illumination. An Osram HBO 50 high-pressure mercury lamp and Leica filters A (excitation 340-380 nm, emission > 425 nm) and D (excitation 355-425 nm, emission > 470 nm) were used for UV fluorescence microscopy.

SPECULAR REFLECTION FTIR IMAGING
Specular reflection Fourier transform infrared (SR-FTIR) imaging provides detailed information on the distribution of chemical functional groups in a paint cross-section.

4 The SIMS measurements were performed by Katrien Keune at the FOM Institute AMOLF.
The FTS Stingray 6000 system was used for SR-FTIR imaging experiments. It combines a Bio-Rad FTS-6000 FTIR spectrometer extended with a Bio-Rad UMA-500 IR microscope (nowadays Varian, Inc., Palo Alto, California, USA) and a MCT detector (4000-1000 cm\(^{-1}\) range), which is a 64 x 64 pixels MCT Focal Plan Array system (Santa Barbara Focal Plane, California, USA). Cross-sectional images in a 400 x 400 \(\text{mm}\) area were recorded simultaneously at every mirror position of the step-scan interferometer at a spatial resolution of 6-7 \(\mu\text{m}\). Imaging spectra were recorded at 16 cm\(^{-1}\) spectral resolution, an undersampling ratio (UDR) of 4 and a mirror step rate of 1 Hz. The step distance of the interferometer at UDR 4 was 1.266 \(\mu\text{m}\). Approximately 500 interferosteps were necessary to obtain a spectral resolution of 16 cm\(^{-1}\). The low step rate (1 Hz) allows the frame grabber board in the camera to average 200 images during each step, leading to a high signal to noise ratio (S/N). A zinc selenide (ZnSe) window was used for calibration and as background spectrum. The resulting data set contained 4096 interferograms, one for every pixel in the FPA. Further data processing was conducted using Bio-Rad Win-IR Pro 2.5 software. The Kramers-Kronig transformation was applied to transform the specular reflectance spectra to absorbance-like spectra, which is easier to work with and interpret. Analytical results of the imaging FTIR system are displayed as infrared spectra and false color or gray-scale images. Every spot or pixel in the cross-section image contains an infrared spectrum. A false color or gray-scale plot shows the intensity distribution of a particular absorption band on the surface of the cross-section.

**Single-point Transmission FTIR Spectroscopy**

Single-point FTIR analysis was performed on the above-mentioned Bio-Rad...
Improving the surface quality of paint cross-sections for analytical imaging techniques

Spectrometer with IR microscope, and a single-point Mercury Cadmium Tellurium detector (4000-650 cm⁻¹ range). The selected sample was applied onto a Graseby Specac P/N 2550 diamond cell (Graceby Specac, Orpington, Kent, UK) and analyzed in transmission mode. An empty diamond cell was used as background. All single point spectra were recorded at 4 cm⁻¹ spectral resolution, an undersampling ratio (UDR) of 2 and a mirror speed of 5 kHz. A total of 100 spectra were accumulated to increase the signal to noise ratio (S/N). Data were processed using Win-IR Pro 2.5 software of Bio-Rad.

SIMS Imaging
Secondary ion mass spectrometry (SIMS) provides detailed information on the distribution of both organic and inorganic components in a paint cross-section. The scanning of a primary ion beam over the surface of the cross-section generates secondary ions from the paint sample. A full mass spectrum is measured for every pixel (max. 1 x 1 μm). The static-SIMS imaging experiment was performed on a Physical Electronics (Eden Prairie, Minnesota, USA) TRIFT II time-of-flight SIMS (ToF-SIMS). The surface of the sample was scanned with a pulsed 25 keV primary ion beam from an ¹¹⁵In⁺ (indium) liquid metal ion gun. The pulsed beam was non-bunched with a pulse width of...
20 ns, a current of 600 pA and spot size of around 120 nm. The primary ion beam was rastered over a 250 x 250 μm sample area, divided into 256 x 256 pixels. The surface of the sample was charge compensated with electrons pulsed in between the primary ion beam cycles. To prevent large variations in the extraction field over the large insulation surface area of the paint cross-section, a non-magnetic stainless steel plate with slits (1 mm) was placed on top of the sample. The cross-section was rinsed with hexane to reduce contamination of polydimethyl siloxanes. Measurements were performed in both the positive and negative modes.

**SEM-EDX**

Scanning electron microscopy studies in combination with energy dispersive X-ray analyses (SEM-EDX) were performed on a XL30 SFEG high vacuum electron microscope (FEI, Eindhoven, The Netherlands) equipped with an EDX system with spot analysis and elemental mapping facilities (EDAX, Tilburg, The Netherlands). Backscattered electron images of the cross-sections were taken at an acceleration voltage of 20 kV, at 5 mm eucentric working distance and a spotsize of 3 that corresponds to a beam diameter of 2.2 nanometer with current density of approximately 130 pA. EDX analyses were performed at a spot size setting of 4 (beam diameter 2.5 nm and current density 550 pA) to obtain a higher count rate. EDX mapping settings were 256 x 200 matrix, 512 or 1024 frames, 200 μs dwell time and 17 or 35 μs amplitude time. Samples were carbon coated in a CC7650 Polaron Carbon Coater with carbon fibre (Quorum Technologies, East Sussex, UK) prior to SEM-EDX analysis to improve surface conductivity.

**DTMS**

Direct temperature resolved mass spectrometry (DTMS) is a fast fingerprinting method suitable for the characterization of classes of organic compounds particularly in tiny and complex paint samples: oils, resins, waxes, proteins, carbohydrates as well as certain pigments. The sample is heated and decomposed into characteristic molecular fragments (pyrolysis) that are measured as a function of temperature. This results in volatilization of weakly bound and low molecular weight desorbing compounds at a low temperature and subsequent pyrolysis of polymeric material at higher temperatures. DTMS analyses were performed on a JEOL SXSS102A 4-sector double-focusing mass spectrometer (JEOL-Europe, Schiphol-Rijk, The Netherlands). Samples selected with a stereo-microscope were made into a suspension in a mini-mortar using aliquots of ethanol. The suspension was transferred to the Pt/Rh filament of the insertion probe and dried in vacuum. The probe was then inserted directly into the ion source and heated. The temperature linearly increased from room temperature to approximately 800 °C in two minutes. The components released from the probe are ionized at 16eV under electron ionization (EI) conditions in an ionization chamber kept at 180 °C, and subsequently mass analyzed over the range m/z 20-1000, with a 1-s cycle time. Data were processed using a JEOL MP-7000 data system.
Improving the surface quality of paint cross-sections for analytical imaging techniques

**Improvement of Analytical Data after Re-polishing**

**Franz Ignaz Günther ‘Saint Isidor’ c.1765 (Abbey Church Rott am Inn)**

The paint cross-section from the flesh tone of *Saint Isidor* shows a thin organic intermediate layer in the paint build-up measuring 8-10 μm in thickness (Fig. 1.3b-c, layer 3). In ultra violet illumination, this layer exhibits a bluish fluorescence. Its composition and function were to be solved. Because the layer was too thin and lacked a distinctive color, we were unable to manually separate this layer from the white ground layers underneath and the pinkish paint layer on top. A first attempt to analyze the thin intermediate layer using specular reflection FTIR imaging did not provide any indication of its nature either (Figs. 1.4a-c). An area of 400 by 400 μm (= 64x64 pixels) of the cross-section surface was recorded. The processed data set contains an infrared spectrum for each pixel. Characteristic absorption bands can be selected in the spectrum and imaged as false-color plots showing their distribution in intensity in the cross-section (red = high intensity; blue = low intensity). The infrared spectrum in Fig. 1.4a represents a spot (a pixel is about 6x6 μm) in the organic intermediate layer, but the spectrum does not contain any particular absorption bands, showing merely noise and interference from the layers on top and below. Careful examination of the surface of the cross-section with the light microscope (bright field, without polarizers) revealed many deformations and scratches. It became clear that the organic layer was scoured below the surface because of its softer consistency, as compared to the adjacent pigmented layers, pointing to a wet polishing preparation. Moreover, the whole surface exhibited many non-reflecting dark spots as a result of unevenness.

After improving the surface by re-polishing, a new FTIR data file that contained relevant analytical information was recorded (Figs. 1.5a-c). Fig. 1.5a shows an infrared spectrum of the intermediate layer after re-polishing revealing characteristic proteinaceous features: a broad band assigned to N-H stretch vibration at $c.3300$ cm$^{-1}$ and the combination of two strong, narrow bands at $c.1643$ cm$^{-1}$ and $c.1540$ cm$^{-1}$ assigned to the C=O stretch (amide I) and N-H bending (amide II) vibrations, respectively. The latter overlaps with the carboxylate peak of (converted) lead white present in the adjacent layers. The intensity of the amide I band at $c.1640$ cm$^{-1}$ is plotted in the FTIR image in Fig. 1.5b: the high intensity (red stroke) represents the organic intermediate layer. Imaging the same absorption band in the data set from before re-polishing had not revealed the same concentrations in the organic layer, only noise owing to surface irregularities (Fig. 1.4b). The image of the carbonate absorption band around 1400 cm$^{-1}$ was also significantly improved after re-polishing and displayed a more even distribution (compare Figs. 1.4c and 1.5c). When combining the FTIR results with the EDX elemental maps of lead and calcium (Figs. 1.3d-e), the presence of carbonates in layer 2 and 4 can be more precisely attributed to lead white (basic lead carbonate) and in layer 1 (ground) to chalk (calcium carbonate). This unique multi-layer structure of flesh painting is similar to other sculptures by Ignaz Günther. Indications
for the use of proteinaceous intermediate layers in the layer structure of flesh areas of polychrome sculptures are found in a Spanish treatise from the seventeenth century by Francisco Pacheco [Karbacher 2004; Richter, Schäfer and Van Loon 2006].

The presence of a proteinaceous isolation layer was confirmed by protein selective staining using Sypro\textsuperscript{\textregistered} Ruby [Richter, Schäfer and Van Loon 2006; Schäfer forthcoming thesis]. These staining tests were also able to identify proteinaceous binding media in the underlying lead white (2) and chalk ground (bottom) layers (1), apart from the high concentration in the organic isolation layer. Furthermore, DTMS analysis of isolated material from the flesh layer (4) demonstrated oil components.

To date, we have only successfully identified pure protein layers in cross-sections using SR-FTIR imaging. However, we have not been able to detect protein features in pigmented protein layers containing inorganic pigments such as chalk or lead white [Van Loon and Boon 2004]. This is associated with the limitations of the specular reflection technique. The intensity of the reflected beam is related to the refractive index of the same sample as described by Fresnel’s law. Organic materials have a lower reflectance, as compared to inorganic pigments with higher refractive indices. In the common case of radiation in air striking the surface of a medium with refractive index $n$ at normal incidence, the reflection is given by $(n-1)^2/(n+1)^2$: for an organic material with $n=1.5$ the reflection at the surface is only 4%, while the reflection is 25% for an inorganic pigment with $n=2$. Furthermore, a much lower content of organic material is exposed at the cross-section surface in typical ground and paint mixtures as compared to pure organic layers. For example, in a chalk/glue ground, a higher amount of chalk is present relative to animal glue (a proteinaceous material). We calculated a typical w/w chalk : glue ratio of about 20 : 1(!). Finally, the most important reason for failure may be scattering within the sample (described as sub-surface reflections), which distorts the specular reflection spectrum.

Fig. 1.6 Vincent van Gogh, *Falling Leaves (Les Alyscamps)*, Autumn 1888 (Kröller Müller Museum inv. no. 224). The FTIR transmission spectrum of the varnish shows resinous, proteinaceous and carbohydrate features (right).
This example also demonstrates the potential of specular reflection FTIR imaging for the analysis of organic layers in paint cross-sections. We examined the thick yellowed/browned varnish in a cross-section from an orangey area in Van Gogh’s *Les Alyscamps* (Fig. 1.6). Questions about the composition of the varnish arose during cleaning tests of the painting because the varnish could not be removed with normal cleaning solvents. The cleaning was further complicated by the impasto character of the paint and the
strong sensitivity/vulnerability of the orangey yellow paint that covers large areas of the painting. Previous research demonstrated that the yellow paint is seriously affected by zinc soap aggregate formation, which has resulted in the manifestation of numerous white-translucent masses at the paint surface that have extended/protruded through the varnish in some areas [Van der Weerd et al. 2003].

Isolated samples of the varnish were analyzed using single-point transmission FTIR and DTMS. The FTIR transmission spectrum (Fig. 1.6b) reveals a mixture of natural resin (blue arrows), proteins (red arrows) and carbohydrates (green arrow). DTMS analysis under EI conditions provides evidence for the presence of mastic, a triterpenoid resin, and under CI conditions of starch, a polysaccharide. Proteins were not detected by DTMS. However, the first attempt at determining the different varnish components and their locations within the cross-section using FTIR imaging were unsuccessful, as shown in Fig. 1.7a-b. Imaging the amide I band at c.1649 cm\(^{-1}\) showed a blurred distribution of the proteinaceous material within the varnish layer.\(^5\) Examination of the cross-section surface with the light microscope (bright field, without polarizers) revealed a very roughened and uneven, low-reflecting surface.

After re-polishing the surface, we repeated FTIR imaging measurements. The new results could clearly localize the different varnish components in the cross-section and link them to observed differences in UV fluorescence within the varnish layer. Fig. 1.8d shows the infrared spectrum representing the lower parts in the varnish layer that exhibited a light-grayish fluorescence in UV. The spectrum reveals characteristic peaks of proteins, two sharp peaks at c.1649 cm\(^{-1}\) and c.1547 cm\(^{-1}\) assigned to the Amide I and II (red arrow), as well as a typical carbohydrate pattern in the 1100-1000 cm\(^{-1}\) region due to C-O stretch vibrations (green arrow) [Derrick et al. 1999]. The carbohydrate band at c.1020 cm\(^{-1}\) was difficult to image because it overlapped with strong sulfate and chromate absorption bands from the lead chromate, barium sulfate (barite) and calcium sulfate (gypsum) present in the yellow paint. Fig. 1.8f demonstrates that the highest concentrations of the 1020 cm\(^{-1}\) band occur in the underlying yellow paint layer. The FTIR image of the amide I group at c.1649 cm\(^{-1}\) (Fig. 1.8c) shows a high and uniform intensity in the lower ‘grayish’ area of the varnish. In contrast, the FTIR spectra of the upper part of the varnish, which shows a much stronger UV fluorescence, display peak characteristics of resinous material (mastic), including a strong carbonyl (C=O) stretch at c.1720 cm\(^{-1}\) and bands in the 2900 cm\(^{-1}\) region due to C-H stretch vibrations (Fig. 1.8e, blue arrows).

From the FTIR results, it is concluded that remnants of a protein and carbohydrate mixture are present on the paint surface, sitting in the interstices of the impasto paint.\(^6\) They must originate from an old restoration, probably from a facing applied to protect the paint surface during the lining process (the painting is wax-resin lined in the past). A mastic varnish was applied on top. This new information on the

\(^5\) The first analysis attempt was carried out by Heleen Zuurendonk (AMOLF intern 2003-04) and described in her Master thesis [Zuurendonk 2004].

\(^6\) The presence of protein confirms the conservator’s observation that the varnish is shrinking and tearing off the paint. Personal communication Luuk Struijk van der Loeff, Kröller Müller Museum Otterlo.
Improving the surface quality of paint cross-sections for analytical imaging techniques

JOHANNES VERMEER ’DIANA AND HER COMPANIONS’ C.1655 (MAURITSHUIS INV NO 406)

In the last case study, we will discuss the SIMS experiments of a paint cross-section from Vermeer’s painting Diana and her Companions [Kolfin et al. 2002]. This cross-section was extensively examined in the context of research on metal soap aggregate formation [Noble et al. 2002; Weerd et al. 2002a]. It exposes the layer build-up of the foliage in the background (Fig. 1.9) showing a light ground, followed by a reddish brown underlayer, then a yellow intermediate layer with lead-tin yellow pigment that has formed metal soap inclusions, and finally a blue top layer containing smalt (blue cobalt potash glass). In SIMS experiments, a primary ion beam rasters over the surface and generates organic and inorganic secondary ions from the paint sample. Similarly, with respect to FTIR imaging, a mass spectrum is collected for each pixel (up to 1x1 μm). Hence, spatially resolved information on the elemental composition is obtained and (pseudomolecular or fragment ions of) whole molecules are detected. SIMS reveals detailed information on the composition of the metal soap inclusions situated in the yellow paint layer. These soap masses are usually too small in dimension to be isolated from the paint layer for analysis. A first attempt to analyze the composition of the layers in this cross-section gave rather poor results. We see a blurred total ion image of a selected area of the cross-section (Fig. 1.12a). Additionally, the imprint of a large scratch is visible through the smalt layer. The overall mass spectrum (Fig. 1.10) contains very noisy and broad peaks. Differences in height in the cross-section surface result in small flight time differences of the ions, resulting in peak broadening and poorly resolved mass peaks.

Re-polishing the surface of the cross-section significantly improved the quality of the SIMS data. Fig. 1.13a displays the sharper total ion image acquired after re-polishing. In the same mass range, the mass resolution is improved resulting in smaller peaks (Fig. 1.11). A good example is the peak at m/z 56. The lower mass side of this peak represents iron, which has an exact mass of 55.96; at the higher mass side, an organic fragment is detected at m/z 56.09. In the mass spectrum obtained before re-polishing, these two peaks completely overlap and cannot be distinguished from each other (Fig. 1.10). The SIMS image of this peak visualizes some hotspots, but there is no clear relationship with the layer build-up (Fig. 1.12b). In contrast, in the mass spectrum collected after re-polishing (Fig. 1.11), the two bands are well-resolved. The iron and organic fragment ions are plotted as separate layers (Figs. 1.13b-c): the highest concentration of iron occurs in the reddish brown underlayer, which supports the presence of red ochre in this layer, while the organic fragment is more abundant in the yellow layer, which is richer in oil paint medium. The detection of lead palmitate (m/z 461-63) and lead stearate (m/z 489-91) in the yellow layer (Fig. 1.13d) confirms the formation of lead soap aggregates, and complements the earlier FTIR and SEM-EDX analyses [Noble et al. 2002; Weerd et al. 2002a]. The deposition of discrete tin particles outside the soap masses (Fig. 1.13e) corresponds to observations reported on other
The three case studies discussed in this paper illustrate the importance of surface preparation of paint cross-sections for successful application of analytical imaging techniques. For specular reflection FTIR imaging, the reflecting surface must appear bright, or mirror like, when viewed with the microscope in incident light (unpolarized). Dark lines and spots are indicative of surface irregularities. SIMS is also a surface sensitive technique: secondary ions are generated from the upper atomic layers of the cross-section. Hence, it is to be expected that even very small height differences in the surface and other irregularities in the surface negatively influence the analytical results.

Examples of saponified lead tin yellow paints [Boon et al. 2004]. The map of cobalt (m/z 59) was also greatly improved after re-polishing the surface and now overlaps better with the distribution of smalt particles in the top layer (compare Figs. 1.12c and 1.13f).

**DISCUSSION AND CONCLUSIONS**

The three case studies discussed in this paper illustrate the importance of surface preparation of paint cross-sections for successful application of analytical imaging techniques. For specular reflection FTIR imaging, the reflecting surface must appear bright, or mirror like, when viewed with the microscope in incident light (unpolarized). Dark lines and spots are indicative of surface irregularities. SIMS is also a surface sensitive technique: secondary ions are generated from the upper atomic layers of the cross-section. Hence, it is to be expected that even very small height differences in the surface and other irregularities in the surface negatively influence the analytical results.
Improving the surface quality of paint cross-sections for analytical imaging techniques

Figs. 1.12 (before re-polishing) and 1.13 (after re-polishing) SIMS images of the paint cross-section in Fig. 1.9.
Chapter 1

We suggest a careful estimation of the surface beforehand to evaluate data reliability and help with data interpretation. A good method of evaluating surface quality and observing surface irregularities was to examine the specimen surface with the light microscope in bright field without polarizers (Fig. 1.14). In this manner, specular reflection of the sample is observed.

We also noticed that normal light microscopy and SEM-EDX benefit from surface improvement. In normal light microscopy, a poor surface is partly compensated by saturating the surface with mineral spirits or by using polarizing filters that reduce light scattering and promote image optimization. An absolute plane surface, however, helps with layer interpretation and provides sharper images. The same applies to SEM-EDX analysis. We noted that a higher surface quality enables higher magnification and leads to sharper BSE images and higher spatially resolved elemental mappings.

In our experience, dry polishing the sample as well as the use of a polishing holder to provide even pressure on the sample during polishing are very essential factors to achieving truly plane surfaces. The other factors considered in the paper such as making short straight movements and the use of clean sheets help to further minimize surface artifacts and chemical modifications of the specimen surface. The dry polishing method can be used to prepare new samples, but the three case studies presented in this paper have shown that it can also be applied to improve the surfaces of existing cross-sections and obtain relevant analytical information.

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