Microspectroscopic analysis of traditional oil paint

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Surface defects have been found recently in Falling Leaves (Les Alyscamps), painted by Vincent van Gogh in the autumn of 1888. These defects have been analysed to comprehend their nature and origin. Embedded cross-section and isolated samples of this painting have been investigated by microscopy, infrared spectroscopy, and FTIR-imaging, SEM-EDX, DTMS. The analyses show that the material found in the defects consist of aggregated masses of zinc carboxylates, which sometimes contain zinc white (ZnO). The carboxylic acid part of the zinc carboxylates consist of saturated fatty acids. The paint in which these defects are found contains lead chromate, barium sulphate (baryte), calcium sulphate (gypsum) in an oil binding medium. Traces of zinc were found throughout the paint layer. The mobility of metal soaps in this paint layer was demonstrated by an FTIR study of the paint after squeezing in a diamond anvil cell.
8.1 Introduction

Routine investigation of *Falling Leaves (Les Alyscamps)*, painted by Vincent van Gogh in the autumn of 1888 (Fig. 8.1, Kröller Müller Museum, Otterlo, the Netherlands, inv. no. 224, F486), revealed the presence of small defects in the extended orange regions of this painting. These thousands of surface defects look like small whitish or transparent spots in the paint surface. In some cases, a whitish mass is literally pressed out of a crack in the paint surface (see Fig. 8.2). These extrusions occurred only after the latest varnish application, because the varnish is cracked open by the extruding matter, which is deposited on the varnish surface.

The phenomenon of material protruding from a paint surface has recently been investigated in several 17th century Dutch paintings.\(^{118,152}\) In these paintings, accumulated masses of a whitish material protrude through the surface of paint layers and thereby manifest themselves on the surface of the painting. These so-called ‘protrusions’ clearly differ from the original paint, as they are devoid of pigment particles and have a transparent appearance. Furthermore, they show clear fluorescence upon illumination with ultraviolet radiation. Chemical analysis showed that these transparent masses mainly consist of lead carboxylates, i.e. molecules that contain an ionic bond between lead ions and carboxylic acids. It has been concluded that the metal ions originate from the lead white pigments, which dissolve in the paint layer. Carboxylic acids are formed in paint by oxidation of unsaturated fatty acids\(^{111}\) or hydrolysis of esterified fatty acids. Fatty acids are not immediately available in fresh paint and the time needed for hydrolysis can be several decades.\(^{19}\) The research described in the previous Chapter of this Thesis indicates that hydrolysed saturated fatty acids (palmitic and stearic acid) are the most important carboxylic acids in protrusions found in a 19th century painting. The presence of similar defects in other 19th century paintings has also been found by other investigators.\(^{158,156}\)

The similarities of the 17th and 19th century protrusions to the defects found in the orange paint of *Falling Leaves (Les Alyscamps)* suggests that they are caused by a similar mechanism, and maybe by the same compounds, i.e. metal carboxylates. The present work aims at a verification or rejection of this hypothesis by a detailed analysis of the paint and especially the materials found in the defects.

8.2 Experimental

*Samples*

The paint samples examined in this paper are taken from *Falling Leaves (Les Alyscamps)*, painted in 1888 by Vincent van Gogh (Museum Kröller Müller, Otterlo, the Netherlands, Inv. no. KM224). A summary of the analysed samples is presented in Table 8.1. Their sample positions are indicated in Fig. 8.1. Sample 224/2a is embedded in Technovit 2000L (Heraeus Kulzer, Wehrheim, Germany) and polished with Micromesh® (Scientific Instrument Services Inc.) polishing cloths. Thin samples necessary for transmission FTIR and transmission optical microscopy were obtained by squeezing a sample in a Graseby Specac p/n 2550 diamond cell (Graseby Specac, Orpington, Kent, UK).
Fig. 8.1. Falling Leaves (Les Alyscamps) by Vincent van Gogh, 1888 (Museum Kröller-Müller, Otterlo, the Netherlands. Inv. Km224, F486) (coloured version at the end of this Thesis)

Fig. 8.2. Macro-photograph of a detail in the orange paint surface of Falling Leaves (Les Alyscamps). (coloured version at the end of this Thesis)
**Microscopy**

A Leica DMRX analytical microscope (Leica Inc., Wetzlar, Germany) was used for visual light microscopy. An XL30 SFEG SEM (FEI company, Eindhoven, the Netherlands) equipped with an EDAX EDX system was used for the SEM-EDX analysis. The accelerator voltage of the system was 22 kV. The sample was carbon coated to ensure good conducting properties of the surface.

**FTIR**

FTIR spectra were acquired by a Bio-Rad FTS-6000 spectrometer (Nowadays Digilab, Cambridge, MA, USA), equipped with a Bio-Rad UMA 500 infrared microscope and an MCT detector. Single point spectra were recorded at a spectral resolution of 4 cm⁻¹, a mirror speed of 5 kHz, and an UDR (undersampling ratio) of 2. 100 spectra were accumulated to optimise the Signal-to-Noise ratio (S/N).

**FTIR-imaging**

FTIR-imaging data were acquired using the Bio-Rad Stingray, combining the FTS 6000 spectrometer and infrared microscope mentioned above with a 64 × 64 MCT camera. Analysis of the embedded cross-section was carried out in reflection mode. Reflection spectra were recorded with a 16 cm⁻¹ spectral resolution, a step-scan frequency of 1 Hz, and an UDR of 4. The spectra were transformed to absorbance-like spectra by the Kramers-Kronig transformation, which is part of the Bio-Rad Win-IR Pro software. Transmission spectra were recorded using the same apparatus at a spectral resolution of 8 cm⁻¹. The different spectra in the data-sets were clustered using the projection-method described in Chapter 2 of this Thesis. This algorithm calculates the similarity between a single spectrum selected from the normalised data-set and the other spectra in the data-set by means of a dot product. Spectra with a high similarity are clustered and the location of three clusters is visualised using RGB-plots. The (not-normalised) spectra within a single cluster are subsequently averaged to increase the signal to noise ratio. All projection and visualisation algorithms were developed in Matlab 5.2 (The Mathworks, Inc., Natick, MA, USA).

**DTMS**

Samples of typically 20 to 60 μg were homogenised in ethanol using a mini-glass mortar. Aliquots of the obtained suspension or extracted materials were applied onto the analytical filament and dried in vacuo. DTMS analyses were performed on a Jeol SX-102 double focussing mass spectrometer (B/E) using a direct insertion probe equipped with a Pt/Rh (9/1) filament (100 micron diameter). The probe filament was temperature programmed at a rate of 0.5 A/min to an end temperature of about 800 °C. Compounds were ionised at 16 eV under electron ionisation conditions in an ionisation chamber kept at 180 °C. Masses in the range m/z 20–1000 were analysed with a cycle time of 1 second. The results were processed using a JEOL MP-7000 data system.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Position</th>
<th>Pretreatment</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>KM224/2a</td>
<td>Cross-section</td>
<td>Embedded</td>
<td>SEM-EDX Imaging-FTIR</td>
</tr>
<tr>
<td>KM224/4</td>
<td>Paint/protrusion</td>
<td>Diamond cell</td>
<td>FTIR, Imaging-FTIR</td>
</tr>
<tr>
<td>KM224/5</td>
<td>Paint</td>
<td>Diamond cell</td>
<td>FTIR, Imaging-FTIR</td>
</tr>
<tr>
<td>KM224/6</td>
<td>Varnish</td>
<td>Diamond cell</td>
<td>FTIR</td>
</tr>
<tr>
<td>KM224/prot</td>
<td>Protruded material</td>
<td>Diamond cell</td>
<td>FTIR</td>
</tr>
<tr>
<td>KM224/relin</td>
<td>Relining material</td>
<td>Diamond cell</td>
<td>FTIR</td>
</tr>
</tbody>
</table>

Table 8.1. Overview of the dissected samples analysed in the presented study.

Fig. 8.3. Microscopic images of cross-section KM224/2a, taken from KM224. (A) Visual light microscopy. The numbers in this image indicate the positions where single point EDX spectra have been recorded. (B) Fluorescence microscopy of this cross-section. (see also the coloured version at the end of this Thesis)
8.3 Results and discussion

8.3.1 Microscopy

The transparent masses were observed in the extensive orange paint areas in the painting by optical microscopy (Fig. 8.2). This orange paint contains many of these defects, especially in the thicker parts of the paint layer. In some cases, the transparent material completely stands upright through a crack in the paint layer. More regularly, the transparent material is seen in a slight elevation in the paint. Sample 2a was taken to include one of these defects and includes some of this whitish material. Optical microscopy of cross-section KM224/2a (Fig. 8.3a) shows a thick (~150 μm) bright orange paint layer on top of a transparent dark ground layer (~30 μm). Two large transparent globules and several smaller dark orange particles are visible in the paint. The globules can be seen clearly upon UV-illumination of the sample (Fig. 8.3b), as they are highly fluorescent, contrary to the surrounding paint. The orange paint layer is thicker near the positions of the globules, suggesting that the surface of the paint has been pushed upwards due to the volume increase of these globules. The globules are not covered by paint, which explains their visibility on the surface of the painting. The fluorescence image shows a light orange structure along the edges of the aggregate, which indicates a sparse presence of pigment particles in this region. The inverse effect, a brighter area in the paint near the aggregates and the ground layer, is also observed. This effect is due to the penetration of fluorescence light into the paint layer.

Cross-section KM224/2a was investigated by SEM-EDX to obtain a higher spatial resolution and allow elemental analysis. A scanning electron image (backscattered electrons) is displayed in Fig. 8.4A. The orange paint is visible as a bright layer, indicating the presence of heavy atoms. The ground layer, varnish layer and the transparent globules are visible as darker regions. A detailed structure is present in the bigger globule on the right. The elemental composition of this cross-section was investigated by single point EDX and EDX mapping. The different EDX plots are shown in Figs. 8.4B-I. The element maps and the backscattered image are obtained in a single measurement, so the images comprise exactly the same area. The bright orange layer contains high amounts of lead (Pb) and chromium (Cr) with a very similar distribution (Fig. 8.4B-C), which indicates that this orange paint layer contains a lead chromate pigment. Barium (Ba) is found in discrete particles in the paint layer (Fig. 8.4D), suggesting the presence of barium sulphate (baryte, BaSO₄). Unfortunately, this map cannot be correlated to the map of sulphur (Fig. 8.4E), as the intense X-ray emission of Pb is very close to the S emission lines. This causes a high background signal throughout the paint layer and completely masks the baryte particles. The barite identity of these particles was confirmed by single point EDX measurements. The particles discernible in the sulphur plot (Fig. 8.4E) do correspond perfectly to the Ca particles in the paint layer (Fig. 8.4F), suggesting that small quantities of calcium sulphate (gypsum, CaSO₄) are present in the paint. Calcium (but not sulphur) is also found in the ground layer, most likely due to the presence of calcium carbonate.

The transparent globules contain carbon (C), zinc (Zn), and oxygen (O). The presence of C suggests that the transparent masses contain a relatively high percentage of organic material. This image further indicates the presence of a third, smaller globule near the ground layer (arrow in Fig. 8.4I). Zn is present in all three globules, but has the highest abundance in the bigger one on the right. A closer examination of this big transparent part shows the presence of two separate fractions. The centre part of the protrusion shows the combined presence of Zn and O. This part
Fig. 8.4. SEM-EDX of paint cross-section KM224/2a.
(A) Backscatter SEM image;
(B)-(I) EDX-maps for different elements, as indicated in the figures.
is also visible in the backscatter SEM image (Fig. 8.4A) as a highly structured region. The left and right sides of this globule contain less Zn and O, but a clearly higher abundance of C (Fig. 8.4I). This globule clearly contains two different fractions: a mainly organic part and a part that contains more inorganic materials. The most likely inorganic material present is zinc oxide (ZnO). The EDX-plot in Fig. 8.4G further shows that Zn is present throughout the paint layer, albeit it in a lower abundance compared to the transparent globules. The presence of Zn in these areas was confirmed by a single point EDX measurement.

### 8.3.2 Imaging-FTIR

The elemental analysis indicated the abundant presence of organic materials in the protrusion areas. The same embedded cross-section was investigated by FTIR-imaging to yield a more specific chemical description. The obtained imaging data-set was processed by a clustering algorithm to enable a fast and easy distinction between different areas in the sample. This algorithm quantifies the similarity of all spectra in the imaging data-set to a single, user-selected spectrum. The quantified similarity can be presented as a score-plot. Fig. 8.5A presents the score plots for three different regions: paint (presented in red), ground (green), and embedding medium (blue). The obtained information on the location can easily be used to combine the corresponding spectra in order to obtain a single spectrum with a high S/N (signal to noise ratio) that is representative for the complete cluster. An averaged spectrum of the embedding medium area, outlined in blue in Fig. 8.5A is presented as the lower spectrum in Fig. 8.5C. While not directly important in the analysis of the paint, this spectrum is kept as a reference to recognise a potential smearing layer of embedding medium on top of the sample. The green colour in Fig. 8.5A represents the ground layer. The absorbance maximum of the carbonate peak in the corresponding spectrum (Fig. 8.5C, 1419 cm\(^{-1}\)) exceeds 5 and is truncated to ascertain the readability of the other spectra in Fig. 8.5C. The presence of carbonate confirms the presence of calcium carbonate, as was already indicated by the SEM-EDX results (see Fig. 8.4F). The spectrum shows a small absorption at 1658 cm\(^{-1}\), which can be assigned to a proteinaceous binder, most likely animal glue. Unfortunately, the amide-II absorption, which would confirm this assignment, is masked by the carbonate absorption. The carbonyl absorption (1743 cm\(^{-1}\)) is not expected in a glue layer. It can be assigned to dislocated glycerol esters from the paint or wax esters introduced during the relining of the painting. Contamination by embedding medium seems unlikely in this case, as the embedding medium was found to absorb at 1728 cm\(^{-1}\) rather than at 1740 cm\(^{-1}\). Furthermore, the other embedding medium peaks (1072, 1149, 1234 cm\(^{-1}\)) are absent.

The orange paint is represented in red in Figs. 8.5A and B. Most of the absorptions in this spectrum are due to organic moieties, as the inorganic lead chromate pigment has no active infrared absorptions in the analysed spectral region. Furthermore, this pigment needs a relatively large amount of oil (20–25\%) to form a workable paint.\(^{170}\) The CH vibrations (2931, 2862 and 1458 cm\(^{-1}\)) indicate the presence of aliphatic materials, while the absorption at 1740 cm\(^{-1}\) is again assigned to glycerol or possibly wax esters. The intense absorption at 1543 cm\(^{-1}\) and the shoulder at 1400 cm\(^{-1}\) are characteristic for metal carboxylates. The exact position of the asymmetric carboxylate peak at 1540 cm\(^{-1}\) indicates a zinc carboxylate,\(^{145}\) but the presence of other carboxylates cannot be excluded. The absorption at 1064 cm\(^{-1}\) is due to BaSO\(_4\), which is present throughout the paint layer with a dispersion finer than spatial resolution of FTIR-imaging. Some
larger lumps of baryte particles can be resolved, and these are represented in green in Fig. 8.5B. The corresponding spectrum ('sulphate' in Fig. 8.5C) shows an intense (truncated) sulphate absorption (1072 cm\(^{-1}\)). The presence of both finely distributed and coarser baryte particles is confirmed in the EDX map in Fig. 8.4D.

The blue-coloured parts in Fig. 8.5B show that the reflectance infrared spectra of the transparent globules are clearly distinguished from the spectra of the normal paint by the applied clustering method. The most notable difference is the complete absence of sulphate absorptions (1064 cm\(^{-1}\)) in the spectrum of the protrusion. Furthermore, the asymmetric metal carboxylate absorption (1404 cm\(^{-1}\)) is a distinct peak, instead of a shoulder. Finally, the CH stretch absorptions appear to be intenser and slightly shifted to lower energy (2924 and 2851 cm\(^{-1}\) instead of 2931 and 2857 cm\(^{-1}\)). These shifts and peak broadening are assigned to oxidation in the paint layer, which obviously did not take place in the transparent globule (cf. Chapter 5 of this Thesis).

### 8.3.3 Manually isolated samples

The possibility to study embedded paint cross-section by FTIR-imaging provides a powerful and versatile method to investigate paint at a relatively high spatial resolution. The spectral quality of the results is however compromised as a result of the reflection mode of data collection, as shown in Chapter 3 of this Thesis. Therefore, several samples were manually isolated and investigated by transmission FTIR and DTM S to complement the results obtained by reflection FTIR-imaging. The sampling positions of the different samples are indicated in Fig. 8.1.

The infrared spectra of materials separated manually from *Falling Leaves (Les Alyscamps)* are shown in Fig. 8.6. The upper spectrum in this figure is isolated material from a transparent globule. The spectrum (A) shows aliphatic CH vibrations at 2924, 2851 and 1468 cm\(^{-1}\). The obtained spectrum is similar to the spectrum obtained by reflection FTIR (Fig. 8.5C). In the transmission measurement, a number of narrow peaks can be resolved for both the asymmetric (1593, 1551, and 1532 cm\(^{-1}\)) and the symmetric (1410 and 1400 cm\(^{-1}\)) metal carboxylate vibrations, due to the higher spectral resolution of the measurement. The transmission spectrum of isolated paint (KM224/5) shows large absorptions for PbCrO\(_4\) (856 cm\(^{-1}\)) and BaSO\(_4\) (1102 cm\(^{-1}\)), ester (1739 cm\(^{-1}\)) and hydroxyl (~3400) groups, all of which are smaller or completely absent in the isolated globule (top spectrum). The aliphatic absorptions in the paint are slightly shifted to 2931 and 2857 cm\(^{-1}\), while a clear fingerprint of metal carboxylates (1551, 1413 cm\(^{-1}\)) is found.

An additional chemical analysis of sample KM224/5 was obtained by DTMS. The results of DTMS measurements are summarised in Table 8.2. The ratio of palmitic and stearic acid in KM224/5 indicates the use of walnut oil. However, the use of the more expensive walnut oil for a yellow area would be surprising. It is therefore assumed that the P/S ratio of the oil is due to a mixture of cheaper oils or is affected by use of additives, a common practice during the 19th century. Bees wax, also found in the paint layer, might be one of these additives. However, its presence in the paint layer can also be explained by impregnation of the bees wax introduced during the relining of this painting. The ions indicative for lead and sulphur are due to the lead chromate pigment and the barium sulphate filler. The presence of carbon dioxide ions can be explained by the decarboxylation of metal carboxylates. The presence of potassium in the paint is confirmed by EDX, but its source is unknown.
Zinc soap aggregate formation in ‘Falling Leaves (Les Alyscamps)’ by Vincent van Gogh

Left-hand image: Fig. 8.5. Imaging FTIR of KM224/2a. The spectra in the FTIR data-set were clustered by the projection algorithm on the basis of their high similarity (See Chapter 2 of this Thesis). The locations of the clusters are highlighted in the score-plots. (A) Score plots of three different clusters showing the paint layer (red), the ground layer (green) and the embedding medium (blue). (B) Score plots of three different clusters showing the paint layer (red), sulphate-rich parts in the paint layer (green) and the aggregate (blue). (C) Mean spectra of each of the clusters shown in A and B. (see also the coloured version at the end of this Thesis)

Fig. 8.6. Transmission FTIR spectra of manually separated samples from KM224, prepared in a diamond anvil cell, show spectra of isolated material from (A) an aggregate, (B) the paint layer, (C) the relining material, and (D) the varnish.
The relining material is identified as a mixture of bees wax and diterpenoid resin. Wax is indicated by narrow aliphatic peaks at 2932, 2857, 1476, 1463, and 721 cm\(^{-1}\) in the FTIR spectrum (Fig. 8.6) and by the observation of peaks at m/z 592, 620, 648, 676, 704, and 732 in DTMS (Table 8.2). The presence of the aged diterpenoid resin is indicated by infrared absorptions at 1693, 1613, 1263, and 1175 cm\(^{-1}\) and by mass peaks at m/z 257, 285, 302, 315.

The varnish layer (KM224/6) is sampled on a position where the uneven varnish layer is relatively thick and allows physical separation. The lower spectrum in Fig. 8.6 is recorded from this sample. Metal carboxylates, which are present throughout the paint, are not observed in this spectrum, indicating that the sample was well separated from the paint layer. This spectrum indicates the presence of a resin (1250, 1130, and 1047 cm\(^{-1}\)) and shows extensive oxidation (OH at ~3300, C–O at 1100–1300 cm\(^{-1}\)). Analysis by DTMS indeed showed the presence of triterpenoids.

Sample KM224/4 was squeezed in the diamond anvil cell to allow transmission FTIR. Figs. 8.7AB show visual light and fluorescence microscopic images of the sample after squeezing. The sample clearly shows three different regions, numbered 1-3 in Fig. 8.7A. These regions were measured individually using a diaphragm in one of the image planes of the infrared microscope. The location of the diaphragm in the different measurements is indicated by the coloured squares in Fig 8.7A.

Region 1 represents the varnish layer, as it is completely transparent and contains no scattering particles. Manual sampling of the thin varnish layer is difficult, but this layer can very well be analysed after squeezing of a larger sample. The spectrum of region 1 (Fig. 8.7C) suggests the presence drying oil, as indicated by the characteristic glycerol-ester triplet at 1170, 1244 and 1110 cm\(^{-1}\). The oil containing varnish on this position is remarkably different from the isolated triterpenoid varnish (lower spectrum of Fig. 8.6) and suggests that different kinds of unpigmented layers are present. These different unpigmented layers might have been applied during successive varnish applications. However, the oil part can also be explained by the presence of a nourishing or oiling-out layer. A more accurate observation of the fluorescence image of sample KM224/2a (Fig. 8.3B) seems to confirm the presence of two different layers on top of the paint layer, as the fluorescing resin layer seems to be separated from the paint layer by an intermediate layer. However, more samples would be needed for a definite interpretation of these results.

Region 2 represents the paint layer, as it has a dark colour in transmitted light (Fig. 8.7A), which indicates scattering and absorption by pigment particles. The infrared spectrum obtained for this region is similar to the paint spectrum (KM224/5) displayed in Fig. 8.6, and shows a clear chromat absorption at 854 cm\(^{-1}\). The spectrum of region 3 is similar to this spectrum, except for the absence of inorganic materials (sulphates and chromates) and a broadening of the absorptions around 1500 cm\(^{-1}\). It can therefore not be assigned to materials from one of the transparent globules, in which these absorptions are clearly narrower (Fig. 8.6A). Furthermore, the spectrum is very different from the spectra of the varnish layers shown in Figs. 8.6D and 8.7C (part 1), and the spectrum of the ground layer shown in Fig. 8.5. The most likely explanation for this layer is therefore that it has been squeezed out of the paint layer by the pressure that has been applied in the diamond cell. This extruded area 3 was further investigated by FTIR-imaging.

Imaging-FTIR of this sample (KM224/4) indicated that this area (nr. 3) is not homogeneous.
**Table 8.2. Interpretation of the results of DTMS on different samples taken from Falling Leaves (Les Alyscamps).**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Observed masses (interpretation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KM224/5</td>
<td>256 (palmitic), 284 (stearic), 592, 620, 648, 676, 704, 732 (bees wax), 206-208 (Pb), 64 (S2O2), 44 (CO3), 39 (K)</td>
</tr>
<tr>
<td>KM224/6</td>
<td>123, 191, 248 (triterpenoids)</td>
</tr>
<tr>
<td>KM224/relining</td>
<td>257, 285, 302, 315 (diterpenoids), 592, 620, 648, 676, 704, 732 (bees wax)</td>
</tr>
</tbody>
</table>

**Fig. 8.7. Microscopy and transmission FTIR spectra of a manually separated, inhomogeneous sample KM224/4).**

(A) Visual light microscopic image of the sample after squeezing in the diamond cell. (B) Fluorescence image of the same sample. (C) Infrared Spectra of the regions 1-3 indicated in A. (See at the end for a coloured version.)
Fig. 8.8. Imaging-FTIR of KM224/4 (same sample as Fig. 8.7). The spectra in the FTIR data-set were clustered by the projection algorithm on the basis of their high similarity (see Chapter 2 of this Thesis). The locations of the clusters are highlighted in the score-plots. (A) Score plots of three different clusters showing the areas 1, 2, and 3 (see Fig. 8.7a) as red, green and blue respectively. (B) Score plot of the clusters showing the upper and lower part of area 3 (See Fig. 8.7a). (C) Averaged spectra of the clusters shown in Figs. 8.8A and B. (see also the coloured version at the end of this Thesis)
Data processing was performed as described before. The obtained clusters (Fig. 8.8A) correlate well to the visual image shown in Fig. 8.7A and the corresponding spectra (Fig. 8.8C) are comparable to the spectra obtained for the single point measurements (Fig. 8.7C). Unfortunately, the lead chromate pigment absorption (854 cm\(^{-1}\)) is invisible for the imaging system due to the restricted spectral sensitivity of the infrared camera. Fig. 8.8A shows that the top part of region 3 (blue in Fig. 8.8A) did not take part in the clustering. The deviation of the spectrum in this top part was first found using multivariate techniques (results not shown), but can also be visualised by the projection method, as shown in Fig. 8.8B. The corresponding spectra (Fig. 8.8C) show a rather large shift in the energy of the CH stretch vibration. These are positioned at 2943 and 2870 cm\(^{-1}\) in the top part, compared to 2931 and 2858 cm\(^{-1}\) for the bottom part. Furthermore, the asymmetric carboxylate has become a featureless plateau between 1550 and 1600 cm\(^{-1}\), while the symmetric carboxylate absorption (~1400 cm\(^{-1}\)) is not resolved from the CH bending absorption (1462 cm\(^{-1}\)). Similar effects have been assigned to oxidation and polymerisation of the oil binding medium (see Chapter 5 of this Thesis). The material extruded by the paint is thus partly oxidised. The different fractions seem to have separated due to the pressure applied in the diamond cell. The clear and easy separation of the paint materials suggests that a rather high fraction of the paint is flexible or even mobile. This observation is important to explain the mechanism of aggregation that leads to the formation of the various transparent globules. Phase separation, the mechanism proposed as the driving force for the formation of protrusions in the previous Chapter of this Thesis, implies the existence of a mobile fraction. The squeezing experiment clearly shows that such a flexible and mobile metal carboxylate fraction is present in the paint of *Falling Leaves (Les Alyscamps)*.

### 8.5 Conclusions

The transparent material found in the surface defects of *Falling Leaves (Les Alyscamps)* mainly consists of zinc carboxylates. The infrared spectra of the carboxylates contain very distinct and narrow peaks for the CH vibrations. The fatty acids involved are clearly not or hardly affected by the oxidation, which is broadening the absorption peaks in the spectra of paint (Fig. 8.6, cf. Chapter 5). The involved carboxylic acids are therefore most likely saturated, non-polymerised fatty acids. This is very similar to the description of protrusions in 17th and 19th century lead white paints, as described in the previous Chapters in this Thesis. It is therefore concluded that both are formed by a similar mechanism: the aggregation through phase separation of mobile, apolar, saturated fatty acids. In this case however, these fatty acids are not connected to lead, but to zinc ions. The Zn compound found in one of the aggregates consists of ZnO based on the combined presence of Zn and O found in the EDX maps (Figs. 8.4GH), and the absence of characteristic infrared absorptions of sulphates or carbonates inside the aggregates. The combined use of lead chromate and zinc white pigments by Van Gogh is not unlikely, and it has been reported before.17 Nevertheless, zinc white is not necessarily the original source of zinc, as it might very well be derived from other zinc containing compounds in the paint. Possible other sources are the chromate pigment, which can contain small quantities of zinc chromate in addition to lead chromates. Furthermore, white vitriol (zinc sulphate) might have been used as a drier.1 Lithopone, a mixture of barium sulphate and zinc sulphide, is less likely as
a zinc source, as the distributions of Zn and Ba do not show any correlation.

The Zn carboxylates are not only present in the aggregates, but appear to be abundantly present throughout the paint layer. In fact, the differences between the infrared spectra of the aggregate and normal paint are small (Figs. 8.6AB). The main differences are the presence of inorganic materials (baryte, 1102 cm\(^{-1}\), lead chromate 856 cm\(^{-1}\)), and a higher amount of intact glycerol esters (1739 cm\(^{-1}\)) in the paint. Furthermore, a higher level of oxidation in the paint is indicated by the absorption at 3100–3500 cm\(^{-1}\) and a broadening of the carboxylate peaks at 1551 and 1413 cm\(^{-1}\).

Despite these small differences, it is clear that carboxylates form a major constituent of the intact paint. The present Zn content of the lead chromate paint seems to be very low (Fig. 8.4G). It is remarkable that the Zn concentration in one of the observed aggregates is higher than in the intact paint. The large unevenness in Zn concentration suggests a certain mobility of zinc compounds. The potential mobility material in the paint was clearly shown by the squeezing experiment in the diamond anvil cell. A solid paint would be expected to result in a crumbled, but reasonably homogeneous layer. Instead, clearly separated areas were found, which shows that part of the metal soap fraction was squeezed out, indicating its mobility. The high amount of mobile materials observed in this study can be explained by a relatively high amount of oil needed to make a workable paint from chromate pigment (> 20–25% \(^{17}h\)).

Direct indications for the mobility of metal carboxylates have not been found in the previous Chapters, in which lead carboxylates have been investigated. It is indeed very well possible that the metal ions might have a profound effect on the properties of the metal carboxylates. In fact, similar effects have been observed in partly neutralised ionomers. These properties also explain the differences in the visual appearance between the Zn and Pb aggregate material. The higher mobility might very go along with a higher pliability of the Zn carboxylates and thereby explain the squeezing out of the aggregated material.

The mobility of the paint materials can be further increased during varnish application. The effect of the triterpenoid varnishes themselves is considered small, but the fluids used to apply the resin might very well accelerate the phase separation by an increase in the mobility of the materials. The varnish application of Falling Leaves (Les Alyscamps) might thus have acted as a trigger in the growth of the aggregates.

The aggregates have a profound impact on the visual appearance of the painting due the extensive expansion. A small calculation indicates that complete transformation of ZnO (\(M = 81.4, d = 5.6\)) to zinc palmitate (\(M = 575.4, d = 1.10\)) leads to a volume increase of factor 36. This large volume increase explains the extensive damage that zinc soap formation can have on a painting. Unfortunately, the clustering of saturated fatty acids and soap formation cannot be reversed. However, it might be possible to reduce the velocity of the formation of these aggregates by lowering the temperature and minimising the exposure to moisture and solvents.
8.6 Acknowledgements

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