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TECHNICAL PAPER

# IMAGING FTIR SPECTROSCOPIC INVESTIGATIONS OF WOOD: PAINT INTERFACE OF AGED POLYCHROME ART OBJECTS

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**Most infrared spectroscopic investigations of painted art objects so far focused on the study of pigments or binding media. Only a few works involved studies of the wooden carrier. In this work the damaged medieval altar from the St. Bartholomaeus Church in Recknitz, Northern Germany, was studied. The research focused on the IR spectroscopic investigation of its wood and ground layer.**

**Cross sections of 10 µm thickness were made to enable studies in transmission mode. The appropriate method for microtoming was investigated. FTIR imaging with high spatial resolution was carried out using a FPA detector consisting of 64 x 64 single detectors. In combination with an IR microscope an area of (267 x 267) µm² could be measured at once.**

**FTIR imaging turned out to be a useful technique to investigate the wood-ground interface. The measured spectra were evaluated using univariate (e.g. displaying the intensity of one band) and multivariate data analysis. The data evaluation was supplemented by the multivariate methods cluster analysis and principal component analysis. Both methods showed clearly the separation of the main components of the part of the studied altar (wood, animal glue, chalk) as well as localized changes in the IR spectra of the wooden carrier.**

## 1 Introduction

Vibrational spectroscopy, especially IR spectroscopy, offers a large variety of applications in the study of art objects. The used spectroscopic methods cover reflection techniques like specular reflection,[1-8] diffuse reflection[9,10] and attenuated total reflection[1,3,9] as well as different transmission techniques. For the IR transmission spectroscopy KBr pellets[1,6,11] and a diamond anvil cell[1,2,8] are used. The investigation of thin sections can be done with laterally resolved techniques like FTIR mapping and FTIR imaging.[1,6,7]

So far the IR spectroscopic investigations have focused on the study of pigments and binding media of art objects. Only a few works involved the study of the painted wooden support of the art work.[12]

In this work especially the wood-ground interface was analysed. The investigations were done on a heavily damaged medieval altar from the St. Bartholomaeus Church in Recknitz, Northern Germany. This 500 years old altar is currently being restored at the Dresden Academy of Fine Arts.[13] The altar was stored from 1851 to 1993 under very humid conditions which caused heavy deterioration, e.g. intense flaking off the paint on the whole altar. To examine possible changes in the wood-ground interface, the lower layers of the altar - wooden support, animal glue isolation and chalk-glue preparation; attached to each other or separated - are analysed with IR spectroscopic methods and compared with reference samples.

To study ageing processes in the wood, changes on the wooden surface and the penetration of the animal glue into the support, the IR spectroscopic measurements have to be done with a high spatial resolution. The best quality of spectra was achieved in transmission mode but therefore the preparation of thin sections was necessary. To stabilize the thin sections an appropriate embedding medium needed to be applied. The embedded samples were cut into a micron scale thickness and measured on an IR sample carrier. Other techniques like Golden Gate ATR, KBr pellets and the diamond anvil cell were used to complete the measurements. The spectra were evaluated using univariate and multivariate data analysis.

## 2 Materials and Methods

### 2.1 IR Spectroscopy

#### 2.1.1 Spectrometers

Different techniques and spectrometers were used to collect the spectral data. Most of the measurements were done using a Bruker IFS 66/s spectrometer. It is attached to a Bruker Hyperion IR microscope (15x magnification in visible and IR region) with a movable sample table. The measurements can be done in reflection or transmission mode using a MCT (mercury cadmium telluride) single detector or a FPA (focal plane array) detector consisting of 64 x 64 MCT single detectors. Using the microscope an area of (267 x 267) µm² can be measured at once, leading to (4 x 4) µm² resolution with the FPA detector. 23 accumulations were used for the FTIR images. The spectra were recorded with a resolution of 4 $cm^{-1}$ in the range of 950-3950 $cm^{-1}$.

The Golden Gate ATR and KBr pellet measurements were done using a Nicolet 210 spectrometer. The spectra were recorded in the wavenumber range of 650-3950 $cm^{-1}$ and a resolution of 4 $cm^{-1}$ with 1000 and 100 accumulations, respectively.

#### 2.1.2 Sample carriers

The ideal carrier for the thin sections has to be well cleanable and transparent in the visible and infrared region. Concerning the transparency KBr carriers would be consistent with the requirements but KBr is a rather soft and water soluble material. $CaF_2$ carriers combine a high resistance to water and scratches with transparency in the visible region. Unfortunately $CaF_2$ is only penetrable for IR radiation in the range of 1050-4000 $cm^{-1}$. The FPA detector cuts off at 950 $cm^{-1}$, which means only 100 $cm^{-1}$ are lost when using $CaF_2$ carriers. Therefore, these carriers are preferred.

Another type of a sample holder is the diamond anvil cell. The sample can be flattened by pressing the two parts of the cell together leading to a better spectra quality. One has to keep in mind that the samples may be damaged by this process and only an area of (0.8 x 0.8) mm² can be flattened at once. Therefore, this technique was only used in special cases.

#### 2.1.3 Data processing

The FTIR images were evaluated using the Matlab based home made program SpecEval.[14] First of all the spectra were linearly baseline corrected using manually selected reference points. A filter was applied to exclude spectra with too high absorption values. Afterwards a minimum-maximum normalisation was applied. Either the most intense band of the whole spectrum or a manually selected band was set to an absorption of one. The spectra were evaluated using univariate data analysis (selecting the intensity at one wavenumber) or multivariate data analysis (cluster analysis, principal component analysis).

### 2.2 Samples and sample preparation

For comparison some reference samples consisting of primed oak wood were prepared. Either fresh or 100 years old oak wood was used as a support. An isolation of animal glue (Kremer Pigmente, Germany) and an animal glue mixed with Rügener chalk (Kremer Pigmente, Germany)

preparation was added. The reference samples were compared to the samples from the altar. No samples containing all layers were available, separated parts were used instead. The altar samples included samples from the wooden support, the used animal glue and some samples of paint flakes (Figure 1).

While plain wood could be cut without additional modification, the primed reference samples and all altar samples needed to be stabilized using embedding media. Different embedding media were tested regarding their cutting properties. Technovit 2000 LC® (Kulzer, Germany) combined easy preparation with sufficient cutting properties and was therefore used for preparing the thin sections. Cubes of around 1 cm length were created in the embedding process and cut to about 10 µm thickness using a stainless steel microtome (Jung, Germany).

## 3 Results and Discussion

### 3.1 Reference Spectra of Animal Glue, Chalk and Wood

The spectra of the components need to be discussed in order to enable a differentiation between the various components (Figure 2).

To avoid any interference while studying all possible bands from the reference samples, appropriate embedding media free preparation techniques had to be applied. The spectra were recorded in transmission mode to ensure comparability with thin section data. The best spectra were obtained from





Figure 1: Altar samples (A) picture of the whole altar from Recknitz, (B) paint flake samples, (C) aged glue samples, (D) part of the left wing of the altar (reverse side) with sampling areas of wooden samples (Photographs: A. Schlegel).

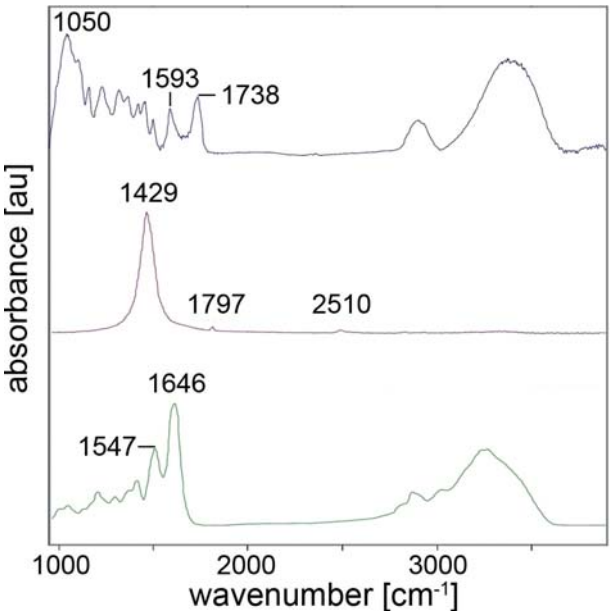


Figure 2: Reference spectra of wood (top), chalk (middle) and animal glue (bottom).

the thin section (wood), the diamond anvil cell (animal glue) and KBr pellet (chalk).

Animal glue is hydrolyzed collagen and therefore shows typical protein vibrations like the so called amide I (1646 $cm^{-1}$, mainly C=O stretching) and amide II (1547 $cm^{-1}$, C–N–H deformation + O–C–N stretching) band.[15] Chalk shows typical calcium carbonate bands like the antisymmetric stretching vibration of $CO_3^{2-}$ (1429 $cm^{-1}$) and combination bands (1797 $cm^{-1}$, 2510 $cm^{-1}$).[16] In contrast to the aforementioned wood contains more than one chemical compound. The main wood components cellulose, hemicellulose and lignin show different bands leading to a rather complex wood spectrum. The bands at around 1050 $cm^{-1}$ can be assigned to C–O stretching vibration of all components while the aromatic stretching vibration at 1593 $cm^{-1}$ can be assigned to lignin and the C=O stretching vibration at 1738 $cm^{-1}$ to hemicelluloses.[17]

### 3.2 Reference Sample

For a reference sample consisting of primed 100 year old oak wood four images are given in Figure 3.

The red square in the microscopic image (Figure 3a) covers an area of (267 x 267) $\mu m^2$ from the microtome slice. Different layers can be optically distinguished. White areas represent holes in the sample.

The same area was exposed to IR radiation and each of the 4096 detector pixels gave a whole IR spectrum. For univariate analysis the intensity of one band of interest was displayed (red=absorbance 1, blue=absorbance 0). Figure 3b shows the intensity at 1646 $cm^{-1}$. This band can be assigned to the amide I vibration of the protein. The picture clearly indicates the isolation containing animal glue.

In Figure 3c the spectra of the white marked region in Figure 3b are displayed. Each spectrum has the colour of the detector pixel it belongs to. In comparison to the reference spectra of the components the blue spectra indicate the presence of wood only (blue arrows) whereas the red spectra in addition indicate the presence of both chalk (green arrow) and animal glue (red arrows).

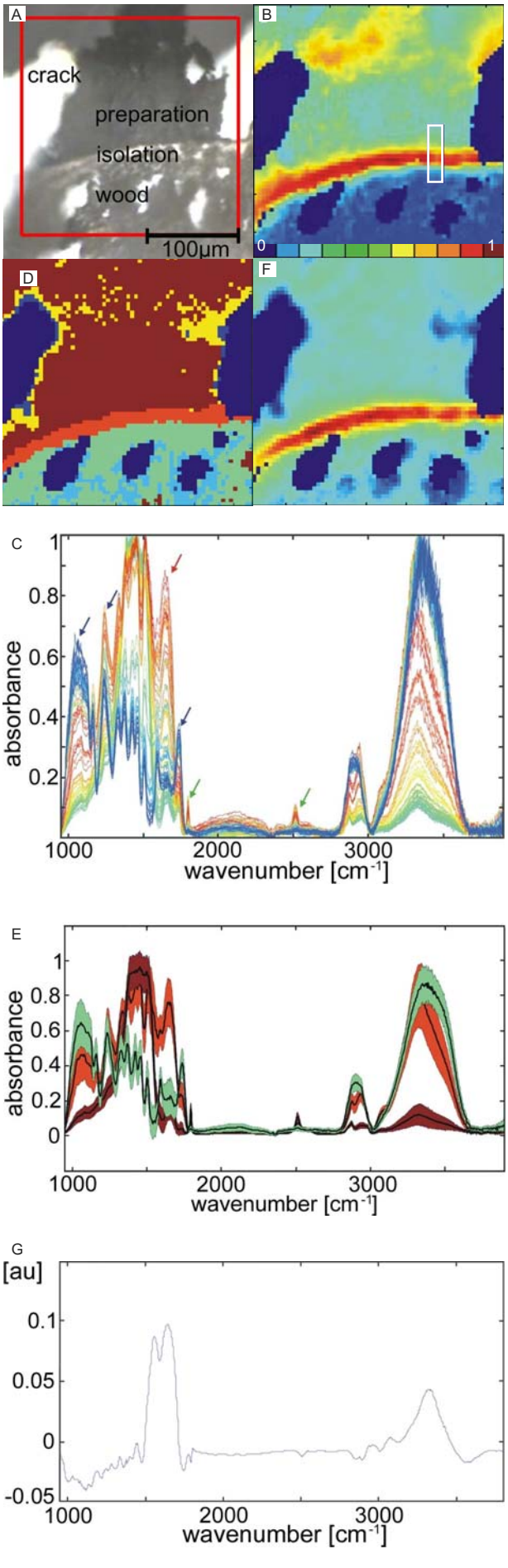


Figure 3: FTIR imaging of reference sample (primed 100 year old oak) and evaluation: (A) microscopic image, (B) univariate analysis: intensity at 1646 $cm^{-1}$, (C) spectra of the white marked region in (B), (D) multivariate analysis: cluster analysis, (E) average data (spectra) of the clusters in (D), (F) multivariate analysis: principal component analysis, variance explanation given by principal component 3, (G) loading plot of principal component 3.

The data cube, consisting of the pixel position, the wavenumber and the absorption value can be further evaluated using multivariate data analysis methods like cluster analysis. In cluster analysis similar data in the data cube, which means similar spectra, are assigned to the same cluster. The number of clusters ("components") can be varied. A separation into five clusters (five different colours in Figure 3d) was chosen. Thereby the different layers could be separated easily. The average spectrum of the animal glue cluster (orange spectrum in Figure 3e) shows as expected high values at the amide I band (1646 $cm^{-1}$).

The PCA (Principal Component Analysis) is another option to analyze a data cube. The redundancy in the data cube is reduced by extracting PCs (principal components) that explain most of the variance of the spectral data. The *score plot* shows in which part of the image the selected PC is found. The *loading plot* contains its "spectrum". E. g. PC 3 contains the information of the animal glue as clearly visible in its score plot (localization, Figure 3f) and loading plot (amide I and II band, Figure 3g).

### 3.3 Wooden Altar Samples

The evaluation results of the reference sample spectra qualify the procedure also for the altar samples. Therefore, one of the questions concerned the detection of a residue of animal glue on damaged wooden altar samples. The aged altar wood showed problems with stability but around twenty appropriate sections from different areas of the samples could be cut.

A selected area of the altar sample (red square in Figure 4a) was measured using FTIR imaging. The image was further evaluated by univariate and multivariate data analysis. For the univariate analysis all spectra of the selected area (white square in Figure 4b) were displayed (Figure 4c), for the multivariate analysis the same area was used for a PCA. An increase of intensity at 1547 $cm^{-1}$ and 1646 $cm^{-1}$ (black arrows) can be found in the spectra (Figure 4c) and the loading plot of PC 3 (Figure 4d). These wavenumbers can be assigned to the amide I and amide II band, indicating the presence of animal glue. The results could be verified by ATR-FTIR measurements (Figure 4e), which where done on surface samples of the altar and cover an area of 1 $mm^2$. It can be stated that the animal glue is clearly visible in this larger area of the surface but only in two of the 10 µm sections of the altar, in contrast to other 18 samples where no protein could be detected by

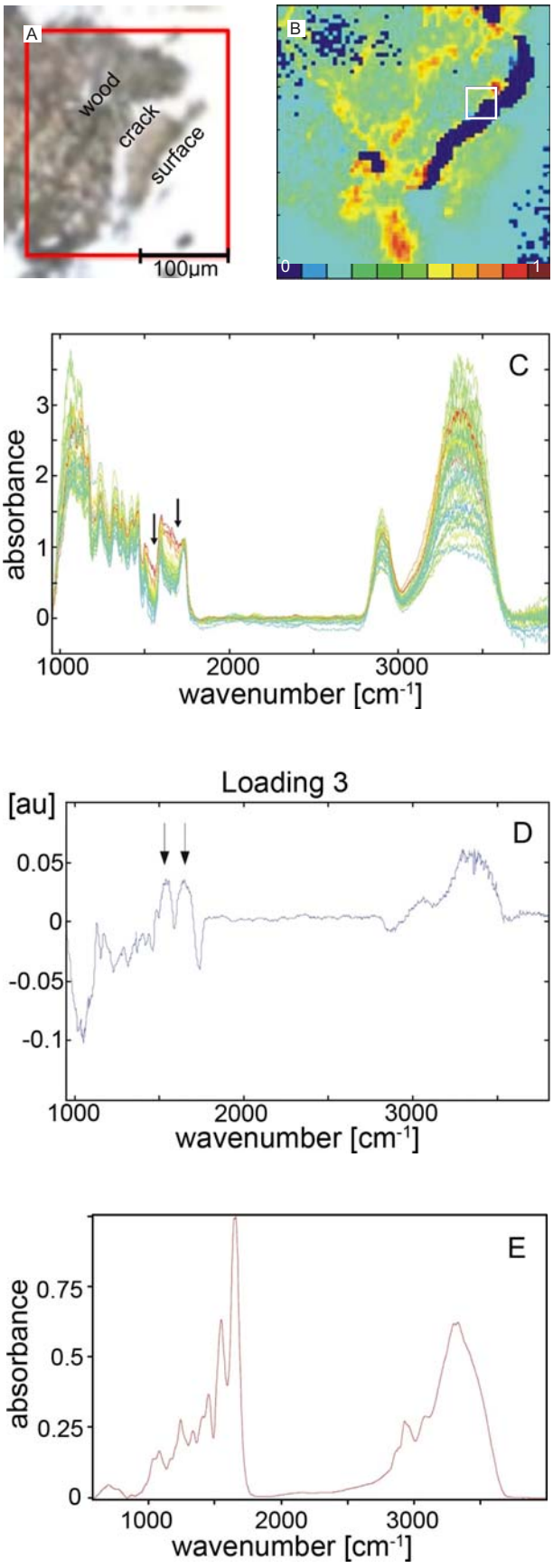


Figure 4: FTIR imaging of a wooden altar sample and evaluation: (A) microscopic image, (B) univariate analysis: intensity at 1646 $cm^{-1}$, (C) spectra of the white marked region in (B), (D) principal component analysis: loading plot of principal component 3, (E) ATR spectrum of altar surface.

FTIR. The obvious low concentration may cause the heavy flaking of the paint.

### 3.4 Glue and Paint Flake Altar Samples

The aged animal glue samples were measured using the diamond anvil cell and compared to the reference animal glue. The spectra looked very similar, only small differences in the intensities could be found. A locally restricted difference (particle diameter about 20 µm) showed the presence of impurities (spectroscopically assigned to $SiO_2$) in the aged animal glue sample.

The paint flakes were prepared as microtome cuts and KBr pellets. The spectra revealed no hint of the binding agent animal glue within the paint from the altar. This may be due to either low concentration or decay of the binder. The poor mechanical condition of the paint flakes may be due to the low concentration of binding agents. No other method for confirmation of binder was applied, however. In contrast the animal glue could be easily identified in the freshly prepared reference samples.

## 4 Conclusions

It could be shown that FTIR imaging in the transmission mode is a suitable method for analysing painted wooden art objects. The high lateral resolution allowed the spectroscopic analysis of structures in the lower micron scale at the wood-ground interface. Distinct changes in the wooden carrier and the distribution of the animal glue could be studied.

The necessary cutting process is not easy for thin layer samples; cracks in the sample can often not be avoided. Nevertheless, appropriate samples can be cut using the right microtoming equipment.

Analysing the FTIR images with simple univariate analysis methods is helpful for known typical bands or components with different absorption behavior. Even so multivariate data analysis was not maxed out, it showed its potential in analyzing a huge amount of data. For a distinct problem multivariate data analysis methods can be refined and thereby even smaller differences in the FTIR images can be distinguished.

## 5 Acknowledgements

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