

# APPLICATION OF MICRO-FOURIER TRANSFORM INFRARED SPECTROSCOPY TO EXAMINATION OF EASEL PAINTINGS

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**ABSTRACT:** The examination of paint fragments from the same easel painting was performed by means of micro-Fourier transform infrared spectroscopy (MK-FTIR). The analysis of chemical composition of each layer visible on cross-section of the chips appeared to be possible in most cases without any layer separation. The identification of small particles isolated from a layer was possible as well. Good reproducibility and high differentiation ability of the method was revealed.

**KEY WORDS:** Easel paintings; Infrared microspectroscopy; Elemental analysis.

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## INTRODUCTION

The technical examination of objects of art is of high importance for conservators, art-historians and curators of art collections. These investigations provide information on the materials and methods that are applied. Art research can help in dating the artwork, in the determination of the provenance or in finding forgeries. Another important subject is the study of degradation processes. The main purpose of any analytical examination is to gain as much information as possible in a non-destructive way.

The analysis of paintings or paint samples takes into account the identification of the pigments and the binding medium. Pigments examination is performed often using X-ray fluorescence (XRF), laser microanalyser (LMA) or relevant techniques [3, 5, 6]. Although separation methods (such as gas chromatography, capillary electrophoresis and liquid chromatography), mass spectroscopy and hyphenated techniques are well suited for the analysis of binding media [9], but the relatively large sample consumption, the expensive sample preparation and the multi-parameter operating conditions are disadvantageous. The spectroscopic methods both infrared and Raman show higher detection limits than several of the chromatographic tech-

niques, but they are more suitable for the non-destructive analysis of binding media in very small samples [2, 4, 7, 8, 10].

Microspectrometry in infrared radiation (MK-FTIR) becomes an important analytical tool in examination of different type of paints. It is an excellent means of determining the chemical composition giving information on the band absorption of functional groups and hence enabling identification of the kind of binders, pigments and fillers present in each layer visible on cross-section of a paint fragment [1, 11, 13]. The great advantage of the application of this technique is the fact, that the preparation of the examined paint sample is simple. Though the fragments of art painting have more complicated structure than car paint chips, nevertheless they may be examined using this technique [12].

In the presented paper an attempt was made to differentiate between paint fragments coming from an Italian painting by means of micro-Fourier transform infrared spectroscopy and scanning electron microscopy with energy dispersive X-ray spectrometry. The analysis of chemical composition of each layer visible on cross-section of the fragment was performed, in many cases without layer separation. The identification of chemical contents of small particles isolated from the particular layer was possible as well. The penetration of some components like glue or natural resins from one layer to another was observed. The results obtained have significant importance for conservation of the painting.

## EXPERIMENTAL

### Materials

Tiny paint fragments from the edges of cracks and losses in a chosen painting ("History of Tucci" of Alvisse de Donati) were sampled with a scalpel. These samples were embedded in wax and cut using microtome into 0.03  $\mu\text{m}$  thick slices, perpendicular to the layers. The samples were placed on the microscope stage of the spectrometer in the infrared beam, the field of view being limited to a single layer and measured with the transmission technique.

If a paint fragment was too fragile to prepare its cross-section, small particles from each layer were extracted with a needle and placed directly on a KBr plate under the infrared microscope.

### Methods

Spectra were recorded on Bio-Rad/Digilab Fourier transform infrared spectrometer FTS 40A equipped with UMA 500 microscope attachment at resolution of 4  $\text{cm}^{-1}$ . 512 scans in transmission mode were collected.

Elemental composition was examined using a JSM-5800 scanning electron microscope (Jeol) equipped with an energy dispersive X-ray spectrometer Link Isis 300 (Oxford Inst.).

All samples were covered with a fine layer of carbon by sputtering in a vacuum sputter SCD059 BAL-TECH.

## RESULTS

Two samples taken from different places of the same painting were examined. Each sample was observed as consisted of 6 layers which were different in terms of thickness, colour and chemical composition. The external layer of sample No. 1 was blue and of sample No. 2 was white. The infrared spectra obtained are presented in Figures 1–6 and the chemical contents of particular layers in both samples are shown in Table 1.

TABLE 1. CHEMICAL COMPOSITION OF PARTICULAR LAYERS IN PAINT SAMPLES

Layer	Chemical composition	
	Sample No. 1	Sample No. 2
I	Resin, oil, egg, CaCO <sub>3</sub>	Resin, oil, egg, CaCO <sub>3</sub> , 2PbCO <sub>3</sub> · Pb(OH) <sub>2</sub>
II	Resin, oil, 2PbCO <sub>3</sub> · Pb(OH) <sub>2</sub>	Resin, oil, egg, CaCO <sub>3</sub>
III	Egg, oil, 2PbCO <sub>3</sub> · Pb(OH) <sub>2</sub> , azurite	Egg, oil, 2PbCO <sub>3</sub> · Pb(OH) <sub>2</sub>
IV	Egg, polysaccharides	Egg, polysaccharides
V	Glue, CaSO <sub>4</sub> · 2H <sub>2</sub> O	Glue, CaSO <sub>4</sub> · 2H <sub>2</sub> O
VI	Glue, CaSO <sub>4</sub> · 2H <sub>2</sub> O, CaCO <sub>3</sub>	Glue, CaSO <sub>4</sub> · 2H <sub>2</sub> O, CaCO <sub>3</sub>

The respective IR spectra of layers IV, V and VI in both samples appeared to be similar to each other, whereas these of layers I, II and III were different qualitatively from each other.

### Layer I

In IR spectra of external layer of both samples (Figure 1) the absorption bands due to natural resin (at 1712, 1460, 1380 and 1030 cm<sup>-1</sup>) and drying oil (at 1734 and 1164 cm<sup>-1</sup>) as well as calcium carbonate (at 1425, 878 and 710 cm<sup>-1</sup>) can be observed. It is possible to distinguish the amide I C = O stretching band at 1656 cm<sup>-1</sup> as well as amide II N-H deformation and C-N stretching band at 1546 cm<sup>-1</sup>. So, the spectra indicates that the paint medium is based on a proteinaceous material such as egg tempera or tempera grassa. However, it can not be excluded that the oil originated from the later conservation of the painting.

Fig. 1. Infrared spectra of layer I in examined paint samples.

It is impossible to identify the kind of oil and resin. The GC/MS method seems to be the best one for this purpose.

IR spectra of both samples indicate a significant difference of the contents of lead white pigment [ $2\text{PbCO}_3 \times \text{Pb}(\text{OH})_2$ ], which is visible in spectrum of sample 2 at  $670$  and  $830\text{ cm}^{-1}$ . Moreover, the concentration of oil in sample 2 seems to be higher than in sample 1.

### **Layer II**

The spectra of both samples (Figure 2) differ in respect of pigment contents. It is possible to identify calcium carbonate ( $710$ ,  $880$  and  $1425\text{ cm}^{-1}$  bands) in spectrum of sample 1 and lead carbonate ( $670$ ,  $830$  and  $1425\text{ cm}^{-1}$  bands) in spectrum of sample 2. Besides, the presence of Amide I and Amide II bands in spectrum of sample 2 can be observed as opposed to sample 1. Remaining components in both samples are the same.

### **Layer III**

Sample 2 (Figure 3) differs from sample 1 in higher concentration of natural drying oil. In sample 1 small particles of blue pigment – azurite [ $2\text{CuCO}_3 \times \text{Cu}(\text{OH})_2$ ] were found.

Fig. 2. Infrared spectra of layer II in examined paint samples.

Fig. 3. Infrared spectra of layer III in examined paint samples.

#### **Layer IV**

The prominent bands at 1658 and 1540  $\text{cm}^{-1}$  revealed the presence of amide I and amide II bands (Figure 4). These features point to the use of

Fig. 4. Infrared spectra of layer IV in examined paint samples.

proteinaceous binder in this instance such as egg tempera or glue. There is a broad band in the region  $1000\text{--}1100\text{ cm}^{-1}$ , typical of C-O stretching and O-H deformation vibrations of primary alcohol groups within polysaccharides.

#### **Layer V**

The main peaks in both spectra (Figure 5) belong to calcium sulphate (gypsum). The weak broad bands might be combined with the glue presence.

#### **Layer VI**

Both spectra are very similar (Figure 6). There are visible strong bands at  $600$ ,  $675$ ,  $1115$ ,  $1620$  and  $1680\text{ cm}^{-1}$  associated with the presence of gypsum. The bands at  $878$  and  $1430\text{ cm}^{-1}$  originate from calcium carbonate. The poorly resolved amide bands might be associated with animal glue. No bands that might be assigned to oil are present.

### **CONCLUSIONS**

The examined samples taken from the same painting were found to be very similar, but not identical. They differed in chemical composition of the first three layers. The differences concerned pigments as well as the medium. These differences result from the kind of applied technique of painting.

Fig. 5. Infrared spectra of layer V in examined paint samples.

Fig. 6. Infrared spectra of layer VI in examined paint samples.

The paint samples can be prepared for examination as cross-sections of the fragments or as small particles isolated from particular layers. Good reproducibility of the applied method was observed.

Thus, the application of the MK-FTIR method enables an easy determination of the kind of the medium and some pigments composing particular layers of painting and so may be useful for identification of its origin. The identification of inorganic groups on the basis of infrared spectra of the paint is very helpful in interpretation of results obtained by the use of elemental analysis. It enables identification of compounds used as pigments. However, the full identification of natural chemical components present in paint binders and other constituents of easel paintings being complex mixtures is possible with the use of both, FTIR and GC/MS methods.

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