Authentication of the Ancient Easel / Paintings Through Materials Identification from the Polychrome Layers

II. Analysis by Means of the FT-IR Spectrophotometry

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This is the second paper belonging to a study concerning the authentication of ancient easel-paintings, on canvas and wood support, from private and public collections, by using the FT-IR spectrophotometry technique for the analysis of the painting materials. Different pigments, egg binders, caseins and animal glue, often found in ancient easel-paintings on wood or canvas, have been used as standards for establishing the ageing rate of the paintings by correlation with the dates presented in the first note. The determination of the degradation rate of the painting materials is an important archaeometric characteristic used in authentication.

Keywords: old paintings, polychrome layers, proteinaceous and lipids binders, pigments, FT-IR spectrophotometry.

Authentication is the essential aspect of a painting which, generally speaking, requires the establishing of its uniqueness and it refers to the particular quality of being originary and original as it has been put into the artwork, and, respectively, to the time patina or to the historical stratification passed from the moment of its creation as an unique artwork, copy or variant, respectively [1 – 4]. The copies can belong to the author himself, to his school (apprentices or followers), to his epoch, but also to some later periods, being painted either with the same artistical technique as the original painting, or with a more modern one, but, nevertheless, as close as possible in its plastic charateristics [5 – 7].

As it has been pointed out in the first paper [1], there exists two groups of attributes which co-operate for the establishing of the authentication as an essential patrimonial element to be taken into account in the scientific investigation of an artwork. Incorrectly, to each attribute there corresponds a so-called specific type of authentication. The age determination, the nature of the materials and the painting technique are reference elements for various types of appraisement which together with the authorship, the market value, the classification, the age and the time patina form the group of the patrimonial elements which characterize an artwork. At the same time, the traces through time, the historic mark and the wear (historic stratification), together with the time patina define the artwork in time and space, thus making it unique [8, 9].

The aim of authentication is indisputable, especially due to the fact that besides the information connected to originality, uniqueness and authorship, we can obtain a series of data regarding the conservation state or the nature of the used materials, the artistic technique and the technology employed into the artwork; all these information allow the accomplishment of the compatibility studies and of the selection of the intervention systems in the active preservation (treatments) or in restoration (consolidations, stabilizations, reintegrations).

There exist nowadays a series of studies [10 – 14] which deal with the determination of some physical, structural and chemical characteristics with a chronological evolution of the component materials of old paintings, characteristics which allow the determination of the age of the materials by using some modern methods such as the IR and FT-IR spectroscopy.

The IR conventional spectroscopy is more and more employed during the last few years to analyze the paintings and especially the binders [15]; however, this method has not always been conclusive due to the complexity of the mixtures and to the small dimensions of the samples.

As compared to the IR technique, the FT-IR spectrophotometry is very fast and has a higher power of resolution. Moreover, very small samples can be analyzed with a μFT-IR spectrophotometer. This is the reason why the FT-IR spectrophotometry is preferred for the analysis of the binders, pigments and inert charges from the structure of the old paintings. This technique allows to carry out comparative studies between the samples of the known naturally-aged binders and the samples taken off from old paintings for which the modifications produced by aging will be rendered evident.

Experimental part

The Sampling and Preparation of the Samples

From the data base of the organic binders samples, naturally-aged from 1976, stored at the OPD Scientific Laboratory, a base organized and indexed by one of the authors of this paper during a specialization period, there have been selected a series of proteinaceous binders (rabbit glue, fish glue, entire egg and casein) which have been considered standard or reference samples [12, 16].

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The real samples of painting material have been taken off from old easel-paintings (canvas and wood support paintings), from private and monastery collections in Romania (Table 1.). Besides these samples there have also been analyzed binder samples taken off from a Rubens painting (in process of being restored in the laboratories of the Opificio delle Pietre Dure), to be more precise, some doubling pastes.

The samples have been finely ground in an agate mortar, then dispersed in potassium bromide, carefully reground in the mortar and spread over under the form of a micro-pellet with a 1.5 mm diameter. The samples have been photometried immediately after being made as pellets.

Spectrophotometry

The IR spectra have been registered in the 200 – 4000 cm^{-1} domain by using a SPECORD M80 Carl Zeiss Jena spectrophotometer while the FT-IR spectra have been registered in the 400 – 4000 cm^{-1} domain by using a Perkin Elmer 1725X spectrophotometer with a 633 nm He-NE lamp, assisted by a Pentium IV computer with a 4 cm^{-1} definition at an average value of 16 scans. Some samples which have arisen a greater interest have been analysed by using a FT-IR Mattson Alpha Centauri spectrophotometer, provided with a water-cooling source, assisted by an IRIS-controlled computer and a DTGS detector. These spectra have been obtained at a 4 cm^{-1} definition at an average value of 64 scans and have been attenuated and differentiated twice.

The obtained spectra have been compared with the reference spectra from the data base of the instrument.

Results and Discussions

The spectra of the samples analysed by FT-IR spectrophotometry have peaks and bands characteristic for each type of the component material. The identifications of the binders and pigments or of the charges which form these samples have been accomplished both by comparison with the spectra obtained for the standard samples, stored in the data base of the OPD Scientific Laboratory in Florence, and on the basis of the specific absorption in IR of the various

Table 1

EXPERIMENTAL DATA OF THE FT-IR ANALYSIS ON THE PAINTING LAYER SAMPLES

No.	General data concerning the analyzed paintings (title, century, sampling area)	Peaks values characteristic for various functional groups (cm^{-1})	Components of the painting layer (charges pigments, binders) and other information
1	"Birth of the Holy Virgin", wooden icon, beginning of the 20-th century, painting layer, ochre background	3600-3200 – OH; 2850; 1650-1720, 1750; 1350-1400, 420; 1100-1000; 880, 690, 600-580.	layer of white ground, based on plaster and animal glue; white-yellowish painting layer, based on Lead white and Ochre; successive layers of varnish, slightly pigmented with Carbon black
2	"Entering in Jerusalim", wooden icon, 18-th century, preparation from the yellow-greenish background	3550-3400 – OH; 2820; 1650-1700; 1120-1160; 680, 610-580.	layer of white ground, based on plaster and animal glue; painting yellow layer, based on Chrome yellow, lightly filled with Carbon black
3	"St. Spiridon", wooden icon, 19-th century, green painting layer from the saint garment	3480-3520 – OH; 2800-2720; 1620-1520; 1400; 1120-1160; 680, 610-580	layer of white ground, based on plaster and animal glue, the area in direct contact with the painting film being impregnated with its oily binder
4	"St. Dimiter", wooden icon, 19-th century, red painting layer from the saint garment	3400-3200 – OH; 2850-2780; 1800-1700; 1420-1480; 1200-1100; 890-700;	layer of white ground, based on chalk and animal glue, partially impregnated with oily binder from the painting film intensively fluorescent under UV rays
5	"Transfiguration", wooden icon, 19-th century, red painting layer from Jesus garment	3550-3400 – OH; 2820; 1650-1700; 1120-1160; 680, 610-580;	layer of white ground, based on plaster and animal glue, filled with black carbon and earths; glue layer
6	"Jesus Christ, Teacher on the Throne", wooden icon, 19-th century, painting layer from the area of Jesus aurora	3400-3200 – OH; 2850-2780; 1800-1700; 1420-1480; 1200-1100; 890-700;	layer of ground, based on chalk and oil ochres, in yellowish tonality; small gold leaf on the sample parts
7	"Virgin Mary with Child", wooden icon, 18-th – 19-th centuries, preparation	3600-3200 – OH **1429.9** (1500-1320) – CH str. (in proteins) **2922.6** – CH str. (in proteins) **875.7** (800-890) – CO_3^{2-}	animal glues; Calcium carbonate; (wooden icon done in tempera with animal glue)
8	"Virgin Mary with Child", wooden icon, 18-th – 19-th centuries, preparation	- **1429.9** (1320-1500) – CH str. (in proteins) - **875.7** (800-890) – CO_3^{2-}	minimun quantity of glue (about 1%) Calcium carbonate
9	"Virgin Mary with Child", wooden icon, 18-th – 19-th centuries, white painting layer	- 3435.7 – H-O-H - **2929.5** – CH (from proteins) - **1541.7** (1560-1520) – peak characteristic for	glue, in mimimum quantity Barium Sulphate (Blancfix) or Litopon (barium sulphate and zinc sulphide)

		NH_2 (amidic bond) from proteins - 1420.6 – CH def. - 1121.4 (1210- 1040), **1081.4** (s), 637,3, 610,7	
10	" Deposition of Christ", canvas painting, 18-th – 19-th centuries, blue painting layer with preparation residues	**- 2920.1; 2851.0** (3000-2800) – CH str. in the yolk proteins **1650.8** – peak characteristic for CO (amidic bond) from proteins **1543.9** – NH_2 (amidic bond) **1424.9** – CH **- 876.2** – CO_3^{2-}	mixed binder from yolk and animal glues (glues residues?) preparation based on Calcium carbonate, blue pigment (artificial French blue) mixed with white based on lead carbonate (canvas with red preparation based on Earths and animal glue); painting technique: one supposes a fat tempera with egg and probably an addition of animal glues (?); the clay residues are probably fragments from the intermediary film between the canvas and the painting layer)
11	" Deposition of Christ", canvas painting, 18-th – 19-th centuries, dark blue painting layer	**- 2919.6; 2850.8** (3000-2800) – CH str. in the yolk proteins **2090.7** (2090-2070) characteristic for the CN group **1646.7** – peak characteristic for CO (amidic bond) from proteins **1541.7** – NH_2 (amidic bond)	mixed binder based on yolk and animal glues (glues residues ?); dark blue pigment (Prussian blue); animal glues residues
12	" Deposition of Christ", canvas painting, 18-th – 19-th centuries, red painting layer	**2926.6** – CH str. from proteins **1635.9** – NH_2 **1429.9** – CO_3^{2-} **1033.8; 913.8; 538.5** and **470.3** – silicates	mixed binder based on yolk and animal glues residues; red pigment (Red earth or bolus?) with red preparation residues based on earths and Calcium carbonate (or Lead carbonate?)
13	" Deposition of Christ", canvas painting, 18-th – 19-th centuries, green - grey painting layer with preparation residues	**2919.8; 2850.6** (3000-2800) – CH str. in the yolk proteins **1651.2** – peak characteristic for the CO group (Amide I band) from proteins **1421.7** (1420-1400) – CO_3^{2-} from calcium white **876.0** (890-800) – CO_3^{2-} **797.6; 539.2** and **469.6** – silicates	mixed binder based on yolk and animal glues (residues); pigment based on calcium white (and probably Carbon black) red preparation based on Red earths (terra rossa)
14	Canvas painting by Rubens, 17-th century, doubling paste;	**2929.0**; 2853.1 – CH str. in proteins 1636.0 –CO from polysaccharides 1620 – H_2O intramolecular **1033.7** – silicates	Starch (dextrine); residues from Venice turpentine; animal glues; residues from Calcium carbonate (the characteristic components of a doubling paste are: wheaten flour, barley flour, etc., molasses, melasă, Venice turpentine, ox
		about **1700, 1448 - ?** **1541.8** – NH_2 in proteins from glues **874.6** – CO_3^{2-}	glue, rabbit glue, fish glue, etc.)
15	"Virgin Mary with Child", wooden icon, 19-th century, red painting layer from the Virgin Mary garment	**2920..9** – CH str. in proteins **1715.6** – CO (COO^-) **1423.3; 875.8** – CO_3^{2-} **1035, 3471.9** – silicates	proteinic material (animal glue?); binder or mixture with a fatty component; Calcium carbonate; silicates (Terra verde?); (wooden icon in the technique of egg tempera?)

functional groups characteristic for the compounds from the structure of the samples.

For instance, one knows the fact that the lipid binders are rendered evident by a characteristic peak at 3425 cm^{-1} (3200-2550 cm^{-1} band) which shows the presence of the oxypolymerized triglycerides from the boiled linseed oil. The un-aged oil has a peak characteristic for the >C=O (from $-COO^-$) at 1740 cm^{-1} group while the aged oil has it at 1720 cm^{-1} or it is displaced towards 1710 cm^{-1} due to the polymerization and the aging processes (1710-1725 cm^{-1}).

Generally speaking, the proteins are caracterized by the following absorption values in IR: 3290 cm^{-1} (s) for >N-H (str.), 2926 and 2854 cm^{-1} (2800 – 3000 cm^{-1} band) for C-H (str.), 1650 cm^{-1} (1630 – 1680 cm^{-1} band) for >CO (Amide I band), 1550 cm^{-1} (1520 – 1560 cm^{-1} band) for $-NH_2$ (Amide II band) and about 1400 cm^{-1} (1320 – 1500 cm^{-1} band) for C-H (def.).

For the *animal glues* (composed mainly of proteins) there has been rendered evident a typical absorption at 1540 cm^{-1} in an area which does not present other signals and the 1520 – 1560 cm^{-1} band for the NH_2 group (Amide II band).

The spectrophotometric identification of the egg yolk is more difficult due to the fact that lipids and proteins are found in its composition. The yolk presents characteristic peaks and bands for the unsaturated esters of the triglycerides which are also to be found in the aged linseed oil. The assigning of the bands will be done, in this case,

by rendering evident the groups specific to proteins, namely, NH (3290, 2080 cm^{-1}), NH_2 (1633, 1538, 1548, 1500 - 1700 cm^{-1}) and –C=O (1651 cm^{-1}, that is, the 1630 – 1680 cm^{-1} range).

For the identification both of the pigments and of the mineral charges contained in these samples there have been rendered evident the bands and peaks characteristic for certain functional groups. Thus, in the case of the lime carbonate (used as charge in the ground) there have been identified peaks specific to the carbonated anion (CO_3^{2-}) while for earths there have been rendered evident silicates (SiO_4^{4-}).

The results given by the IR and FT-IR analysis on samples of painting layers taken off from old paintings in (T%) transmission, in the 400-4000 cm^{-1} range, are presented in table 1.

The data from the IR and FR-IR spectra have allowed the pointing out of the basic components from the various layers of the preparation and of the polychrome film, shown in Table 1, which in a next paper will be correlated with the data obtained by the hystochemical analysis on micro-stratigraphical samples. The data obtained from the IR and FT-IR spectroscopy have also allowed the identification of the modifications undergone in time by materials from a physical, structural, chemical and chromatic view point.

Conclusions

The IR and FT-IR analyses of the pigments and binders used for old paintings on canvas or wooden support have pointed out the chemical modifications of the binders and the presence of some painting materials which have been employed in more recent periods as against the ones which have been initially attributed, thus proving that some attempts for faking them out have been made.

Among them, at the wooden icon "Virgin Mary with Child", initially dated around 1756 according to the conservation card, there has been rendered evident the presence of the Lithopone as white pigment, a mixture of barium sulphate and zinc sulphide, this being an artificial paint used in painting only from 1873.

At the same time, we have succeeded in differentiating the paintings done in the techniques of fatty tempera and the oil ones, respectively, which in many cases are mistaken one with the other due to the varnish or to the natural time patina, these paintings being incorrectly registered in the conservation records.

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