„Alexandru Ioan Cuza” University of Iaşi
Faculty of Geography and Geology
Doctoral School of Chemistry, Life and Earth Sciences

STUDY OF NEW CHARACTERISTICS OF OLD WOODEN ARTIFACTS

PhD Thesis Summary

PhD supervisor:
Prof. univ. dr. Ion SANDU

PhD student,
Raluca Anamaria CRISTACHE

Iaşi

2015

C o n t e n t s

Keywords: wood anatomy, stratigraphy of a painting, deterioration and degradation wood species identification, dendrochronology, MO, μ-FTIR, SEM, thermogravimetry, wiggle matching, pigments, binders, varnishes, *Tillia codata*, *Picea abies*, dendrochronological series

Acknowledgements: This work was funded from POSDRU / 159 / 1.5 / S / 133391 contract, strategic project " Excellence doctoral and post-doctoral programme for training of highly qualified human resources for research in Life, Environment and Earth sciences ", European Social Fund through the Sectoral Operational Programme for Human Resources Development 2007-2013.

Chapter I - WOOND AS A SUPPORT FOR ARTWORK, makes a presentation of the characteristic features of physiological, anatomical, functional and chemical properties of wood to support works of art and defects of growth thereof or features of wood species of interest in dendrochronology.

The annual rings are composed of individual cells being structural elements of wood. In order to accurately identify species and to distinguish wood annual rings, the wood should be known and understood at the cellular level. Also, the physiology of trees is particularly important to understand the link between the environment and the formation of the rings, these being the complex result of a series of assimilation of natural resources, nutrients, by the tree itself. A variety of chemical reactions and cell division produces the annual ring that holds information needed for dendrochronological analyses.

Chapter II - STRATIGRAPHY OF A PAINTING WITH WOODEN SUPPORT presents the stratigraphy of an easel painting on wooden panel, stating wood species used in the making process of various artefacts and detailing the component layers of a painting technique of specific objects studied.

Most times the wood was processed by independent artisans, but are known cases where some painters worked with one carpenter. The panels were made of wood countertops with a thickness between 3-5cm, usually reinforced with wedges or crossbeams. The surface was prepared by planning and sanding with finer smoothing of the top layer [Sandu, 2005]. The ground is the first layer that covers the panel for painting or gilding, being made of animal glue and calcium sulphate or calcium carbonate. Tempera with egg is considered to be the oldest painting technique. It combines pigments with emulsions, which have protective and binding role. Gold leafs are obtained today in different shades and degrees of hardness, 24 carat pure gold being the softest. Tin or silver leafs, which do not stain, they were coloured to mimic gold, in addition to its use in the natural state. Varnish is the final layer that protects against dirt deposited on the surface of the painting, the corrosive gases in the atmosphere, moisture and mechanical deteriorations, providing shine and suppleness to the image.

Chapter III - CONSERVABILITY OF OLD WOODEN ARTIFACTS. DETERIORATIONS AND DEGRADATIONS, is carefully studying the preservation of works of art through the systematic environmental and anthropogenic factors influencing the progress and integrity of art objects and effects of deterioration of physical and chemical degradation of their nature. It details the effects of damage and decay, the most common in old painting easel, based on the typology of these paintings, showing structural components and materials involved in the installation, followed by detailing differentiated results of the action of exogenous factors and those on the endogenous structural and functional components respectively on existing materials, the deepening deterioration and degradation issues on wood from the simple to the complex effects and explaining the mechanisms of evolutionary progress.

Chapter IV - ARCHAEOMETRIC CHARACTERISTICS AND METHODS USED IN AUTENTIFICATION ASSESSMENT, presents an overview of the archaeometric characteristics and methods used in assessing the attributes of authentication, pointing dendrochronological dating methods, radiocarbon, wiggle matching and other methods of analysis and dating of wooden artefacts.

Chapter V - ANALYSIS TECHNIQUES AND METHODS USED ON WOOD ARTIFACTS is establishing the chemical nature and the conservation state of the component materials of ancient paintings on wood, based on an analytical protocol for the investigation of the paint layer by involving modern techniques para-destructive, using: spectral and radiative methods (UV, Vis, IR, XR etc.), chemical methods for separating and identifying components of a mixture, staining reactions (histochemical) specific for some components and others.

Investigation of an historical heritage artwork involves a series of methods, techniques, procedures and operational means consisting in a direct and non-destructive analysis (trace evidence, fingerprint, impressions etc.), followed by the non-invasive with sampling and processing of samples from different structural elements or materials. Non-destructive analysis assumes a direct observation with the naked eye or with optical instruments (magnifiers, microscopes, etc.). Using photographic means, such as the camera or film (visible light, UV or IR through direct and normal lighting ir reflectography) is also mandatory. This category includes the use of techniques such as radiography, reflection colorimetry, X-ray fluorescence analysis of material or form traces (impressions, micropowders, ultrathin films, etc.) which does not require sampling.

Chapter VI - ANALYSIS OF THE CONSERVATION STATE. CASE STUDIES presents the analysis of the conservation state of selected case studies. This chapter contains detailed analysis of each object from historical, style, technique, execution point of view and of the conservation state.

First icon is entitled *Our Lady of Sorrows*, painted in Neo-byzantine style, with dark colors, focusing on the face (Fig. 6.1).

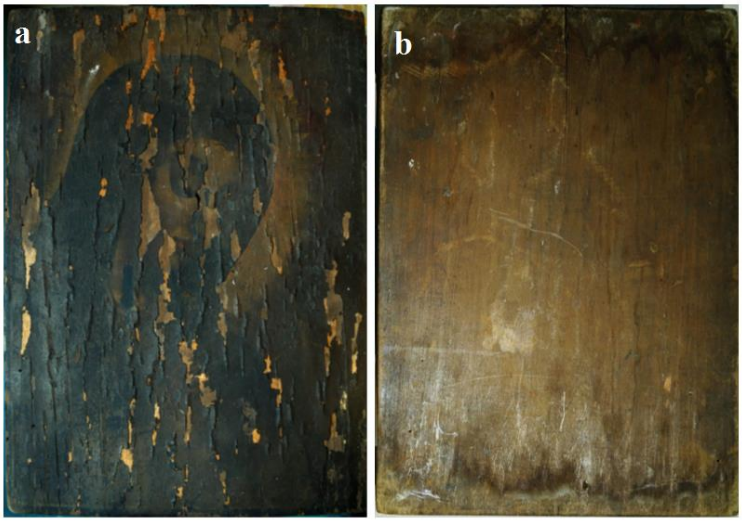

Fig. 6.1. The icon *Our Lady of Sorrows:* a. front, b. back

The painting is done on linden tree panel, cut tangentialy from the trunk, consisting of a single countertop without crossbeams on the back. Dimensionally, the icon is relatively small having 30cm in length, 23cm in width and 2,2cm in thickness. The painting is on the outside of the annual rings. The analysis showed that the surface of the panel was brushed bone glue a thin layer of ground, which didn't manage to create adherance for the painting layer. The presence of gold leaf is reduced to the few fine rays that make up the halo of the Virgin. Pigment film is thin but very compact, the iconographer opting for dark colors, penetrating and shellac varnish. The reverse of the icon is well preserved, unlike the pictorial layer. In terms of integrity it has a vertical crack in the top of the icon, from point of insertion of the nail support. The painting layer is in a precarious state of conservation requiring immediate consolidation, mostly being detached from the base with significant losses.

Second studied painting is the icon *Mother of God Hodighitria*, which is part of a private collection, being painted in egg tempera, in the byzantine style with naive influences (Fig. 6.2).

Fig. 6.2. The icon *Mother of God Hodighitria:* a. front, b. back

Wooden support of the icon is made of spruce, a single countertop without cross beams. A thick ground layer, met in the normal stratigraphic structure of Byzantine icons, is lacking in this case. Classic gold foil of byzantine icons used for the halos is replaced, in this case, by a yellowish-golden pigment. Olifa is the varnish used, demonstrated by the brownish tint of the layer, and its unevenness. The wood panel is in a relatively good structural state of conservation, not affected by loss of timber. The presence of a knot in the icon support led to the formation of a crack crossing the thickness of the panel. Heat is the trigger factor leading to drying the panel, blistering the paint layer, elevation of the knot and its curvature.

The third icon Pentecost, is a small fragment (15.2 × 28,5cm), which was part of a church iconostasis, painted neoclassical style (Fig. 6.3).

Fig. 6.3. *Pentecost* icon fragment, front and back

The wooden support of the icon is carved from linden wood, which burned approximately 50%. The painting layer is covered by a layer of smoke and ashes resulting from burning, it has detachments, blisterings and gaps. The protective coating used originally is dammar.

The icon depicting *Saint Nicholas*, and is part of a private collection, painted in egg tempera, Russian Byzantine style on linden wood panel (Fig. 6.4).

Fig. 6.4. The fourth icon depicting *Saint Nicholas:* a.front, b.back

The wood panel is of linden wood, consisting of three tops bonded together with bone glue. They have straight edges and no plugs, wedges or other forms of binding, being glued on straight edges. The icon is painted in tempera technique, as a binder for the pigments was used egg yolk emulsion.

The entire surface is covered with silver leaf stamped in circular and vegetal patterns, the garments and decorations being painted over leaf. In terms of integrity of the panel, two planks of the panel have separated. Underlying the detachment, which is centrally positioned in the lower part, the left plank was fractured due to poor handling, losing some of the wood on the back. The painting layer has profound gaps along the loosening of the countertops and where the tips of the nails from the beams have passed through the support and painting layer. Also, in the lower area of the icon, the painting layer and the wood are burned. The protective varnish layer is Olifa, an oil-based varnish.

Another group of artefacts studied are some Stardivarius violins, from private collections, from which is presented only one, which has had the agreement of the owner. The violin is not in a very good state of preservation. It was intervened to restore it by installing and removing the covers, which led to damaging of the surfaces (cracks, fractures, and deep gaps) and degradation in the wood support. This hypothesis is strengthened by the presence of coarse traces of glue used by the restorer trying to glue the wooden tops.

Chapter VII - SAMPLING AND PROCESSING SAMPLES FOR ANALYSIS, presents the methodology of sampling and sample preparation for analysis on identification of component materials, author technique, wood species and for the involvement of other instrumental techniques for the determination of new archaeometric or chemometrics features.

Wood sample preparation for cutting with a microtome is a process in several steps, related to the conservation state of the fragment and of the elements to be analyzed under a microscope: the preliminary preparation (getting wood fragments), soaking and embedding the sample in resin (if applicable), cutting and fitting samples on glass slides (optimum sections thickness vary between 15μ and 20μ). To analyze cell structure, the sections, where appropriate (new wood, old wood without fungal infestation, old wood with fungal infestation) are histochemically stained with safranin 1% or picric acid and aniline blue solution, this process requires a pre-treatment with NaClO, followed by rinsing with water, then staining, rinsed with water and alcohol again, and those with fungal infestation after immersion in xylene, are embedded in resin.

Laboratory instrumentation used in sampling of the painting layer, consists of blades, rods, brushes, syringes, forceps with sharp or blunt tip, pliers etc. A modern way of sampling is core drilling, which can be adapted particularly well to study multylaiering. Mechanical sampling of fine microsamples by laser can be done on a glass microscope slide, using an Er:YAG, often used to clean paintings.

Chapter VIII - IDENTIFICATION OF PAINTING MATERIALS AND DETERMINATION OF THE CONSERVATION STATE OF ICONS, presents the analysis of the conservation state and the identification of archeometric characteristics with the help of modern investigation techniques as: optical microscopy (OM), scanning electron microscopy coupled with X-ray spectrometry (SEM-EDX) [Kouloumpi et al., 2007] and infrared spectroscopy (micro-FTIR) for a series of icons of the nineteenth and twentieth century. Referring to the determination of the conservation state, were analysed the effects produced by the action of the microclimate factors, biological agents, including humans, which have deteriorated and degraded the studied icons.

VIII.1 The icon *Our Lady of Sorrows*

The icon entitled Our Lady of Sorrows has a precarious conservation state, the paint layer being in an advanced destabilisation. The panel is quite well preserved, with a slightly bended, having fissures caused by the movement of wood over time, scratches and abrasions at the corners.

Optical microscope analysis has found new information about the varnish, pigments, metal leaf and primer used by the painter. The samples were enhanced from 50x to 500x, and observed under a microscope in reflection mode [*Derrick, 1999*].

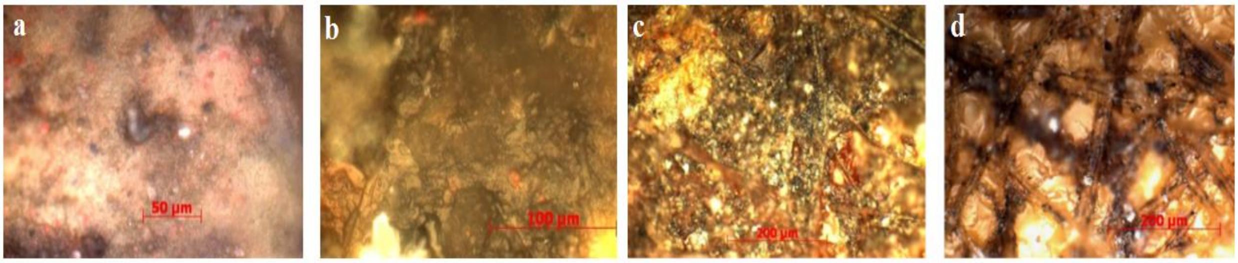

Fig. 8.1. Microscopic photographs of paint layer:
a. halo, b. face, c. background, d. cloak

At a magnification of 200X, the sample from the halo area (Figure 8.1a), has a thin layer of varnish, non-cracked, which in some areas has suffered processes of oxidative fouling [*Sandu et al, 2009*]. Also the varnish has clogged dust and dirt, under it the yellow metallic leaf with high gloss can be seen, placed on a layer of dark brown pigment. Under the thicker layer of varnish from the face (Fig. 8.1b), it can be seen a light coloured pigment, white with ocher. The samples of the cloak and the background were enlarged by 400X, where in the background sample a mixture of ocher, red and brown pigments could be seen (Fig. 8.1.c). In the detail of the cloak (Fig. 8.1d), in an area with partially varnish, a dark colour was seen, a mixture of blue and brown, with particles of red.

The SEM-EDX analysis of all 4 samples collected from the paint layer of the icon, have detected the presence of ground, which cannot be seen macroscopically, meaning that it is a very thin layer with no adherence to the panel which lead to big loses of painting layer. The metallic leaf form the halo rays is visible only under microscope, looking like gold, but the EDX analysis demonstrated that it was used silver leaf covered with concentrated shellac varnish. Some chemical elements as Si, Ca, Al, P, Fe, K, Mg, Na, and O, were detected in all the analysed samples showing the fact that natural earth pigments were used. The EDX analyses of the cloak sample has identified elements corresponding to natural ultramarine blue - $Na_3CaAl_3Si_3O_{12}S_{10}$ made of lapis lazuli, a well know precious stone.

The FTIR spectrum analysis of the cloak indicates that the paint layer contains ultramarine blue, dust and schellac (Annex II, Fig. Ae and f). The bands that appear in the IR spectrum can be attributed, in accordance with the script of the data sampling and as in the literature [*Kaszowskaa et al, 2013; Vahur et al 2010*] as ultramarine pigment, with a very weak and narrow band, with 3 picks: 694cm^{-1}, 657cm^{-1}, 582 cm^{-1} [*Favaro et al, 2012*], confirmed by comparison with the reference spectre of ultramarine blue.

VIII.2. The icon *Saint Nicholas*

The icon Saint Nicholas is painted in russian style with a reduced colour palette, and covered with silver foil in the background. The panel is made of linden wood. Conservation state of the icon is precarious, two of the panel tops have detached, which led to the fracturing of the entire painting, and following an intense Xylophage attack, the wood lost its density and strength. Analysis of the surface paint layer reveals details such as: burned marks at superficial and deep layer, longitudinal fissures parallel to the wood grain, with roof top detachments , elevating of pigment layer in two slopes along the fissure, clogged varnish , darkened, uneven and coarse dirt adherent layer.

With the help of SEM-EDX and μ-FTIR techniques, were identified the following structural elements: sheet of paper, ground, pigments (vermilion, cinnabar, lead white, ochre and carbon black), metallic silver leaf and varnish olifa. The elemental composition identified by EDX shows a rich amount of Pb and Fe, with traces of Ca, S (ground) and other elements (Si, Al, Cl, Mg, Na, K) characteristic to the pigments obtained from natural earths. EDX spectra of the background sample shows a large amount of Al derived from the metal leaf. For the same multilayer sample (background) the mapping of the identified elements has been made (Fig. 8.2), where the arrangement of the silver layer and its detachment can be seen (Fig. 8.2c). Compounds characteristic to the ground, namely calcium (Fig. 8.2e) and sulphur (Fig. 8.2f) are evenly distributed, detachment of the silver leaf being very visible.

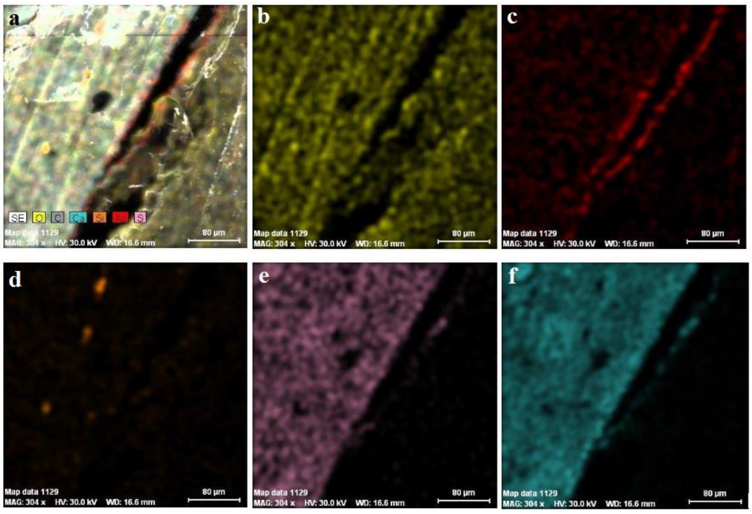

Fig. 8.2. Mapping chemical elements identified in the background sample:
a. the distribution of all the elements, b. the distribution of oxygen, c. the distribution of silver, d. distribution of the silicon, e. the distribution of sulphur, f. the distribution of calcium

VIII.3. Comparative study between artefact components to identify the making process

A comparative study was made between the sheets of paper from three Russian icons, with the same painting technique and making technology: *Saint Nicholas, Mother of God from Kazan and Saint Anastasia*. A first step was the microscopic analysis of the samples (Fig. 8.3.).

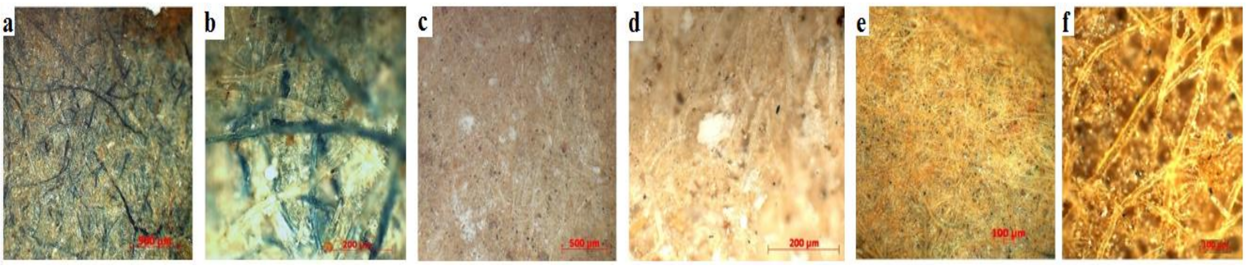

Fig. 8.3. Microscopic images of paper samples (50X-200X):
a/b - Icon of *Saint Nicholas*, c/d - Icon of the *Mother of God from Kazan,*
e/f - The icon *Saint Anastasia*

SEM EDX analysis of paper samples of the icons: *Saint Nicholas, Mother of God from Kazan* and *Saint Anastasia*, revealed in addition to the components of paper and traces of ground and paint. Lead is the only distinctive element present in the sample Lady of Kazan in high concentration (3.64%), and indicates the use of a coating techniques used in the first half of the nineteenth century. Calcium highlights the use of $CaCO_3$ to give brightness and high whiteness to the paper. The presence of K, Al, S in all samples, suggesting the use of alum in processing the paper paste. Trace amounts of Cl are from NaClO (sodium hypochlorite), which was used as a bleaching agent. The identified fillers are: dehydrated calcium sulphate ($CaSO_4 \cdot 2H_2O$), aluminium sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$), talc ($3MgO \cdot 4SiO_2 \cdot H_2O$), rosin and rabbit glue. Following the results obtained from the analysis of the paper samples, the icons belong to the first half of the nineteenth century.

VIII.4. The icon *Coronation of Our Lady*

The icon Coronation of the Virgin is painted in oil technique, in neoclassical style, on a linden panel (*Tilia cordata Mill*) and it was not signed or dated, but after the manner and style of the painter, the icon was painted in nineteenth century. Conservation state of the icon is precarious: the wood panel being embrittled due to xylophagus insect infestation.

The Optical Microscopic analysis has shown layers of ground, pigment, varnish and adhering dirt. The impurities are clogged in the varnish and the painted surface is irregular in all samples analysed. Corroborating the results obtained by SEM-EDX analysis and μ-FTIR the nature of the pigments and primer was identified: the red pigment is a mixture of vermilion, minium and burned sienna; ultramarine blue pigment is and primer - $CaCO_3$.

Chapter IX - IDENTIFICATION OF NEW ARCHAEOMETRIC CHARACTERISTICS IN WOOD presents the identification of wood species of archaeological artefacts that plays an important role in dendrochronological dating, bringing new information on the origin of the object, or can provide another perspective on its authentication.

IX.1. Wood Specie Identification of the icon support *Saint Nicholas*

To determine the cellular structure of the wood and the deterioration and degradation state of the icon of Saint Nicholas, the samples were analyzed by optical microscopy (OM), scanning electron (SEM) and FTIR micro-spectroscopy. The cross-sectional analysis showed that the wood specie is linden (Tilia cordata Mill) a hardwood, with diffuse pore distribution, having no marked difference between the pore sizes, thick walls are gathered in 2-3 radial rows (Fig. 9.1).

In the tangential section the rays appear generally in series of 2 to 4 cells, rarely 5 or 6 series. Height of the ray varies from 10 up to 50 cells or more, the form of the rays are axially-oval, small, and ray expansions are very distinct.

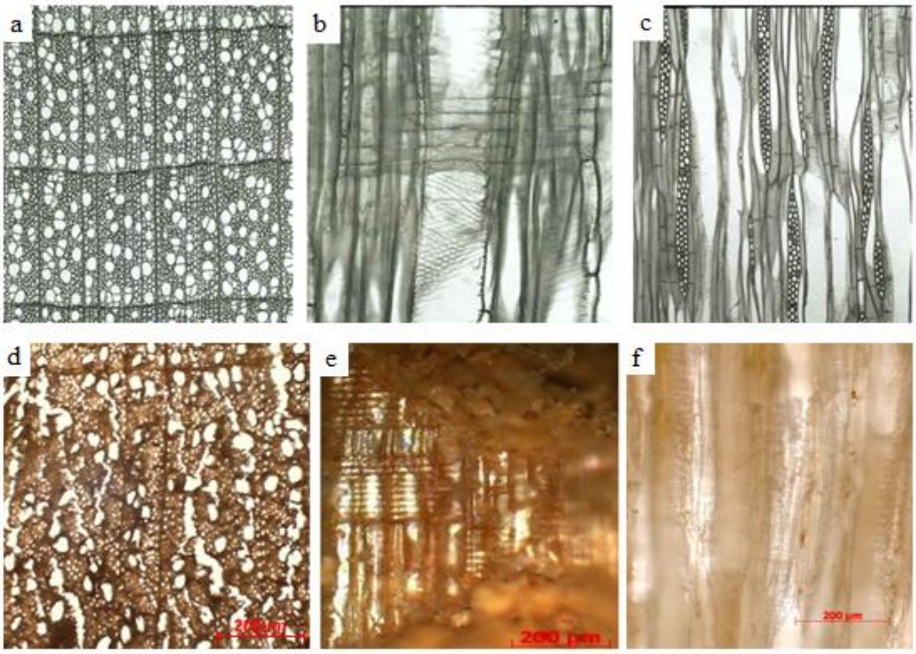

Fig. 9.1 Microscopic sections:

a. transversal (reference) b. radial (reference) c. tangential (reference)

d. transversal (unidentified), radial (unidentified) f. tangential (unidentified)

IX.2. Anatomical study of the wooden panel of *Mother of God Hodighitria* icon

To identify the wood specie of the icon of *Mother of God Hodighitria*, the samples were examined by optical (OM) and electronical (SEM) microscopy, where the following details were observed: the transition from early wood to late wood is gradual, specific hardwood vessels are missing, but are present resin canals surrounded by epithelial cells (Fig. 9.2).

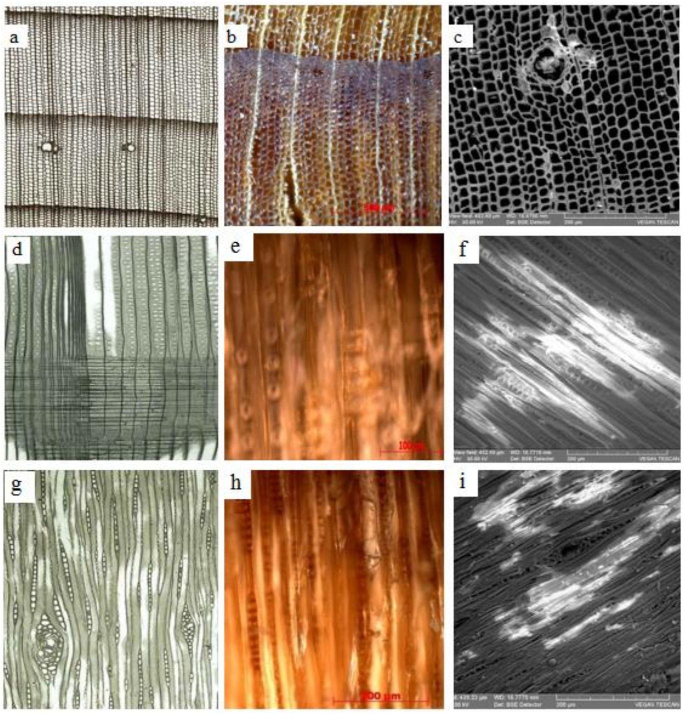

Fig. 9.5. Microscopic sections: unidentified timber (b, e, h), reference images (a, d, g)

SEM micrographs (c, f, i); a, b, c - transversal, d, e, f - radial, g, h, i - tangential

Also, the medullary rays are shown and at a bigger enhancement, the radial parenchymal cells are observed. The vertical resin canals is surrounded by more than 8 epithelial cells which are displayed in longitudinal clusters. The tangential section of the wood expose the tracheids which are long, with sharp edges, consisting of 10 to 25 cells. Identified morphological and anatomical elements in the studied samples belong to the *Picea abies* specie.

IX.3. Deterioration and thermal degradation of the wood support of a nineteenth century painting

To determine the wood specie of the icon fragment representing the descent of the Holy Spirit, burned partly due to a fire, a sample from the back of the panel was analyzed (after removing charred part) by optical microscopy and found that the support is made of linden wood (Tilia cordata Mill.).

Ageing of the linden wood is evidenced by the size and shape of the DTA curve, which occurs at low temperatures the first two intervals (25-180°C, 180-390°C) and, therefore, the increase of the curve at higher temperatures, in the third interval (390-450°C). Both phenomena occur as a result of the structural changes in lignin.

IX.4. Identification of wood species of a Stradivarius violin copy

The most used wood species in violins making are maple (*Acer Platernoids*) from the family *aceraceae*, spruce (*Picea Abies* or *Picea Stichensis*) and ebony (*Diospyros ebenum*).

To identify the wood species used for making of the copy of Stradivarius violin, a sample of the violin front and one from the back, were analyzed; it was found that the face of the violin is made of spruce (*Picea abies Karst*.), and the back of the violin is made by maple (*Acer Platernoids*). From the taken samples only two sections have been obtained: one tangential for the maple sample (Fig. 9.4) and a radial section for the spruce sample.

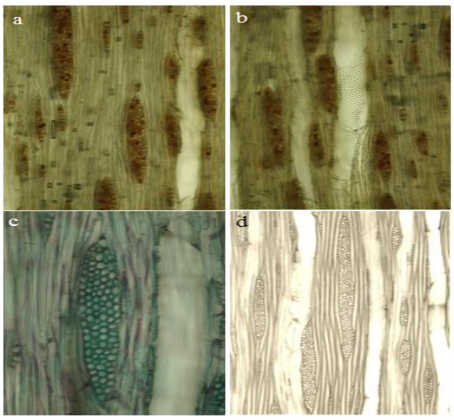

Fig. 9.4. Tangential section of the maple sample:

a. 100X, b. 200X, c. 500X d. reference

According to anatomical atlases for identification of species wood, maple is described as having in cross-section a diffuse pore distribution, with different annual rings [*Conners, 2011; Schweingruber 2007*]. The vessels are solitary, in pairs and in rows up to 6 cell length. Their width is up to 90µm. The vessels have thin walls in tangential section and sap deposits may occur. These are intervasculare and tracheids pits are average (7-8µm), polygonal, alternate, simple perforated plates with three spiral thickenings [*Arno, 1988; Gregory, 1994*].

Chapter X - DENDROCHRONOLOGICAL DATING OF WOODEN SUPPORTS presents the potential application of this dating method on old wooden artifacts.

X.1. Dendrochronological dating potential using Romanian chronologies

It is true there are certain species which prove unquestionably appropriate for dendrochronological analysis, due to their capacity of recording with great precision climate changes, despite growing in geographical regions far away from one another. For purely statistical reasons, dating chances are so much greater as the number of years for comparison is larger; thus, the longer the chronologies are, the more they are representative.

This study is based on highlighting the teleconnection and heteroconnection between certain chronologies in Romania and other chronologies from neighboring countries, all performed on spruce (*Picea Abies*). The statistics and synchronizations were carried out using the PAST4 software, product of SCIEM, by considering the agreement coefficient or GLK for "Gleichläufigkeit" [*Eckstein and Bauch 1969*], t_{BP} or Baillie-Pilcher's t value [*Baillie and Pilcher 1973*], and t_H or Hollstein's *t* value.

Figure 10.1. illustrates correlations between selected synchronizations. Thus, the best synchronizations with *t* values of over 5 are highlighted in Fig. 10.1a, average synchronizations with *t* values of around 3 are shown in Fig. 10.1.b, and synchronizations with chronologies in the Russian Far East in Fig. 10.1c. The best correlations were found between Giumvău (2) and Ocolașu (4), for which the *t* value is 8.66, the two regions being relatively close to each other. These are followed closely by Roncan (6) and Novaci (3), with a *t* value of 5.46, the two regions being at the extremities of the Carpathian Mountains chain. Nonetheless, the chronologies of Giumvău (2) and Zănoaga (7) have no correlation, the *t* value being much too low, 1.87.

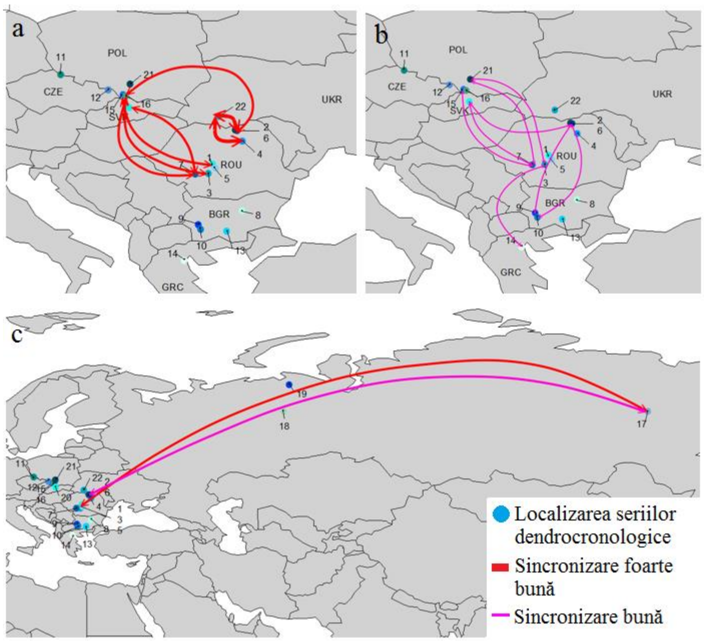

Fig. 10.1. Synchronization of selected chronologies:
a. best synchronizations (red), b. average synchronization (purple),
c. synchronizations with datasets in Asia

X.2 Dendrochronological dating and estimation of the felling date

For crossdating the *Icon of the Virgin Mary Hodighitria,* a rim of the wood panel was exposed; the tree-rings widths were measured (in their entirety?), from the center (pith) towards the exterior (bark), using the OSM software. A total of 26 rings were measured, and the data was analyzed in a *skeleton plot* using the PAST4 software.

The best results from graphical crossdating (Fig. 10.2) were obtained in the case of the Romanian chronology of Ocolașu, for which the agreement coefficient (GLK) was found to have a value of 71.20%, for the cutting year of 1946.

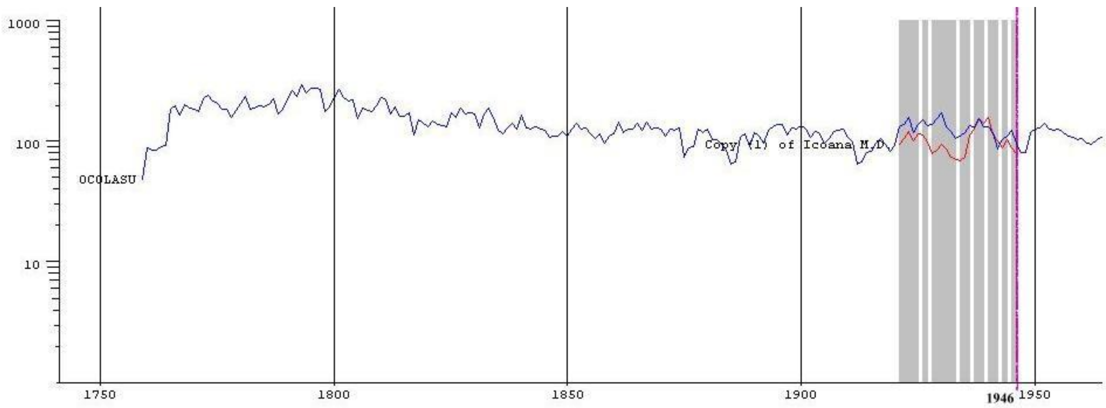

Fig. 10.2. Graphical superposition of dendrochronological curves

The *t* value for the positioning in Fig, 10.2 is 2.95 times too small for being confirmed as conclusive. However, the cutting year of 1946 has been found for other reference chronological datasets as well, by means of graphical synchronization. Despite the low correlation values, the repetitive occurrence of this year suggests that 1946 is the most probable value of the cutting year, the 26 rings proving insufficient for retrieving a conclusive answer.

X.3. Dating a Stradivarius violin copy

For the crossdating of a reproduction of a Stradivarius violin, the workmanship as well as features of the master luthier's authentic violins have been analyzed. Hence, while the customary label of a Stradivarius violin, whether authentic or counterfeited, uses the traditional Latin inscription according to the McKinnley Tariff Act of 1891, copies must also mention the country of origin, information which is missing from the label of the studied violin.

Once the tree-rings were highlighted, they were counted and measured with 0.001 mm precision, using the OSM software (Fig. 10.3). The measuring layouts followed the lines of optimal visibility, beginning from the exterior of the left wood panel, followed by graphical and statistical synchronization.

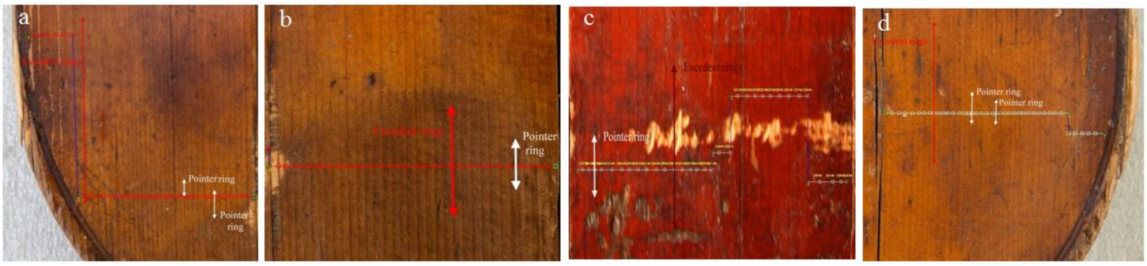

Fig.10.3. Measurements of each ring of the 5 constitutive wood panels of the front of the violin, marking the characteristic years.

The chronology of the violin was compared against the available national and international reference chronologies for *Picea abies*, by means of multiple tests (t_B, t_H, GL). For this purpose, the characteristic years were determined from the performed measurements, and a graphical synchronization with the characteristic years of the reference datasets was attempted. This analysis suggests the year 1719 for an optimal positioning. In this case, and considering the time period required for drying and preparing the wood, most probably the violin was made in 1721.

Chapter XI - IDENTIFICATION OF NEW ARCHAEOMETRIC CHARACTERISTICS IN WOOD, presents the correlation between chemometric characteristics of archaeometric value for wood and pictorial materials.

Therefore, dates of elemental chemical compositions were analyzed, as well as extractable components of wood of different types and ages, for the purpose of chemometric characterization. To that end, two types of wood were considered – linden and poplar, of different age and preservation state. The chemometric study includes measurements of elemental chemical composition (C%, H%, O%, $N_{organic}$%), ash%, humidity% (RH) and pH.

Based on the results of the following ratios C/H, C/O, (C+H)/O, (C+H)/$N_{organic}$, pH/Humidity and $N_{mineral}$/Ash, the plots of the evolution of the aforementioned chemometric characteristics as a function of age, separately for linden and poplar, as well as the information on the extractable components (ratios of extractable components in NaOH 1% at cold temperature (10^0C) and extractable components in cold water (10^0C), extractable in NaOH 1% (10^0C) and extractable in hot water (80^0C), also extractable in ethanol (96%) and anhydrous ethyl ether), as a function of age, separately for linden and poplar, the relevance of these characteristics for their archaeometrical quality was analyzed.

For the linden wood, the 2 chemometric aspects were analysed on 4 samples with different conservation state, taken form artefacts with various ages (between 4 and 198 years). For the first group of arheometrical characteristics, 7 graphs were made, that show gradual evolutions, almost linear; only the ratio between C/O, (C+H)/O, (C+H)/$N_{organic}$, pH/ Humidity and $N_{mineral}$/Ash can be used for arheometric determinations (Fig. 11.1).

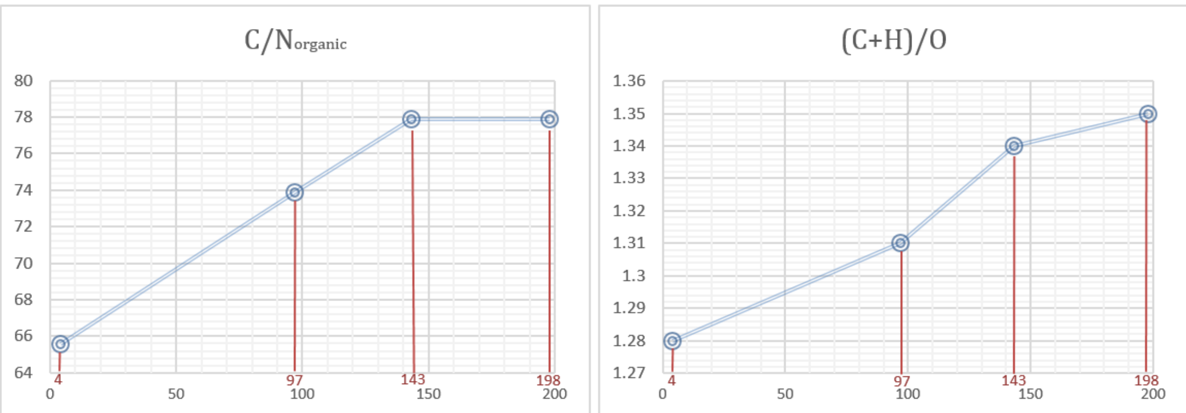

Fig. 11.1. Variation of chemometric characteristics as a function of age for linden wood

Similarly, for the case of poplar wood, based on the chemometrical data, graphs of the evolution of the chemometric characteristics as a function of age were done. Compared to the data for linden, all chemometric characteristics' evolutions exhibit a linear increase, which could allow their use in achaeometric assessments (Fig. 11.2).

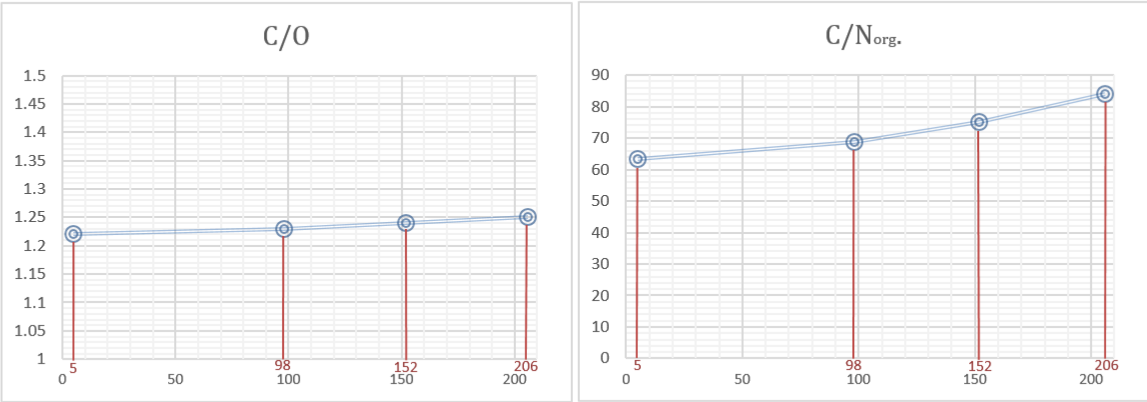

Fig.11.2. Variation of chemometric characteristics as a function of age for poplar wood

Likewise, the chemometrical characteristics for linden and poplar were determined, concerning the ratios between the compositions of extractible components in cold NaOH 1% (10^0C) and extractible in warm water (80^0C), extractible in ethylic alcohol (96%) and extractible in anhydrous ethyl ether (Fig. 11.3 and Fig. 11.4.).

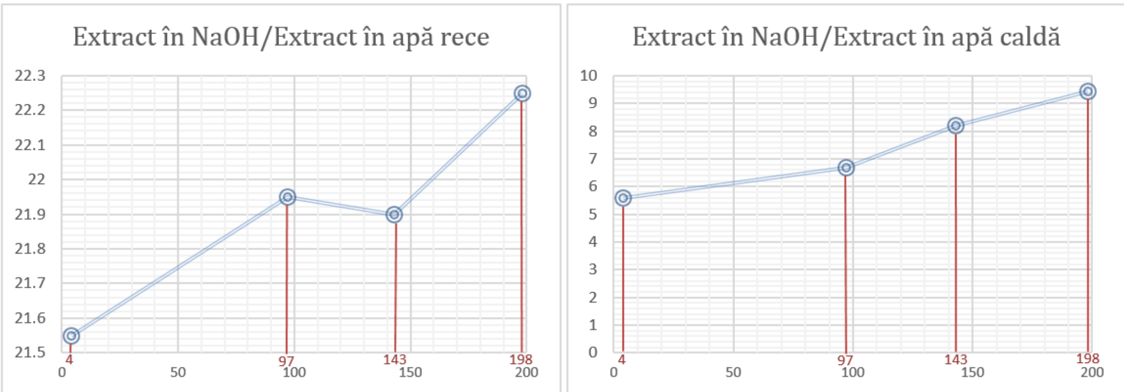

Fig.11.3. Graphs of ratios of extractable components compositions for linden wood.

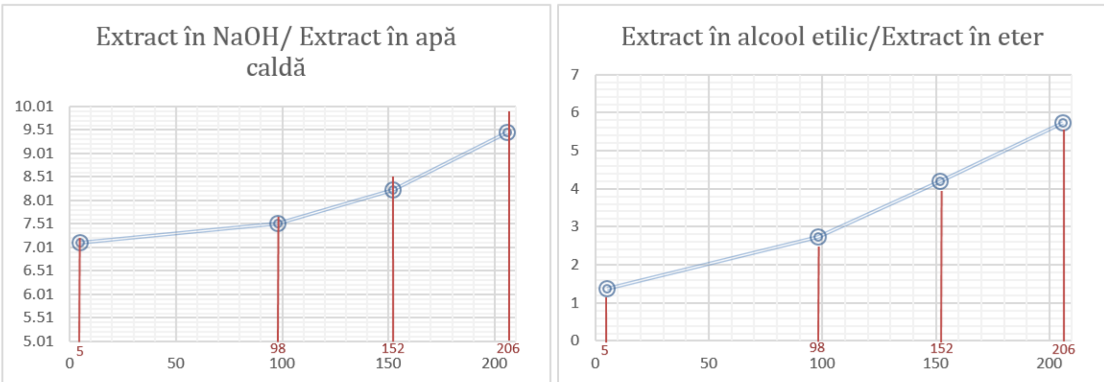

Fig. 11.4. Graphs of ratios of extractable components compositions for poplar wood.

Between the three chemometrical characteristics, the last two can have arheometric value.

Chapter XII - GENERAL CONCLUSIONS

The doctoral thesis entitled "Study of new archaeometric characteristic of old wooden artefacts" was developed based on experimental data and bibliographic research studies regarding new features for archaeometric wooden artefacts, for authentication, museum valorisation and cultural integration. These studies were based on a complex critically analysis, on which a summary of the literature on the current state of scientific research in the following areas was made:

• identification of painting materials and assessment of their conservation state (determining the nature and physical-structural characteristics of wooden artefacts components);

• establishing the interaction between environmental factors and agents on wooden artefacts components by analysing the deterioration, degradation and unwanted deposits on their surfaces;

• methods and techniques involved in the determination of some of the archaeometric characteristics and chemometric charactersitics with archaeometric value;

• microscopic identification of wooden species;

• dendrochronologcal dating of the wooden support;

• identification of new archaeometric features of indigenous wood.

To this end, several priority research directions are addressed:

The first direction is the analysis of biological characteristics of wood and determining of the wood species. With this the dendrochronology wood dating is achieved and put into practice in conjunction with identifying archaeometric features of the other component materials (pigments, binders, varnishes, primers, artistic techniques, the technology of making, subsequent intervention of preservation and restoration) and with the study of art-historical and archaeological sources, used as reference.

Another direction concerns the method of dendrochronological dating and its applicability on the ancient artefacts of wood form the Romanian cultural heritage, in order to obtain data that allows, together with the information obtained by analysing other component materials and the reference source, to determine the age and provenance of the artworks.

The third direction regards the identification of new archaeometric features paying particular attention, to wood, but also chemometric characteristics with archaeometric value.

The goal of the thesis is to focus on fundamental research and applied research in archaeometry for authentication, hoarding and valuing of unexplored or lesser known old wooden artefacts,. It seeks to achieve experimental protocols on selection and taking the study of artefacts, the collection and processing of samples for analysis, proposing modern methods of investigation, involving co-assistance systems and corroborating between interdisciplinary techniques and the use of chemometric features of old wood and archaeometric data and other material constituting wooden artefacts.

In this regard, attention was focused on the one hand on the detailed knowledge of the behaviour of old wood artefacts during displaying, storing or use in various cultural or religious (if applicable) rituals, under the influence of endogenous and exogenous factors by real-time analysis of the evolution of their conservation state and clarification of the mechanism of developmental effects of deterioration of the physical state and degradation of the chemical nature of the component materials, to stop the process of destruction and alteration, while on the other hand, assessing the effect of deposits or inappropriate interventions the could affect the integrity of the old wooden artefacts.

For dating and authentication (determining author / workshop and sourcing of materials) an analysis is required primarily by a group of researchers from several fields: chemistry, physics, biology, history, art, archeology, conservation science, etc. and modern investigation techniques. The dating of a wooden object requires a conjunction between several disciplines, each bringing a range of information on which to obtain a definitive answer.

Wooden artefacts, common in our country, can be dated using dendrochronology, however there are times when this is not enough. It is often required to use a series of chemical, physical-structural and mechanical properties analysis of their components. If a painting or an unknown old icon, it is necessary to first consolidate dynamic damage and stopping biological attacks (if active), and then perform the preservation and restore the support and paint layer, before finally identifying the wooden species and determining the date of the piece, and author if possible. After completing these mandatory steps, the areas of sampling will be selected for analysis, which should be representative. An edge of the panel or a chassis or a frame will be used, which will be cleaned and sanded to identify annual rings. Also, for some large artefacts (eg. coffins, crosses, iconostasis, furniture, craft items or old wooden engineering structures) wooden dome samples are selected, which highlight annual rings of the structure. The annual rings are measured and then placed in a specialized software to carry out a "graphics skeleton" analysis and then use a database of international wood species that will date by overlapping "schedule frames" over a series of reference. With the background for identifying pigments and binders used and other artistic techniques and the technological data of the installation, the artefact will be assigned a time and area of belonging. The wooden artefact offers several annual rings, so much so that the end result is more accurate. The paper presents in detail all these steps in order to obtain reliable results.

All this required assiduous scientific research, consisting first of in-depth study of literature in the field of dating and authentication artefacts of wood, its contributions to art and analysis of ancient paintings easel with wooden stand (icons in tempera poor / fat), but also of stringed musical instruments (violins Stradivarius model). The typological analysis took into account the most common causes of damage and decay, identifying the component materials and their conservation status, followed by complex research on the characterization of the archaeometric and chemometric archaeometric value.

SELECTIVE BIBLIOGRAPHY

1. Abdel-Maksoud G., (2011), *Analytical techniques used for the evaluation of a 19th century quranic manuscript conditions,* **Measurement, 44**, pp. 1606-1607.
2. Acquaviva S.; D'Anna E.; De Giorgi M.L.; Patria D.A.; Baraldi P., (2010), *Physical and chemical investigations on natural dyes,* **Applied Physics A**, **100**, pp. 823-828.
3. Alla A.Q.; Camarero J.J., (2012), *Contrasting responses of radial growth and wood anatomy to climate in a Mediterranean ring-porous oak: implications for its future persistence or why the variance matters more than the mean*, **European Journal Forest Research, 131**, pp. 1537-1550.
4. Bartens J.; Grissino-Mayer H.D.; Day S.D.; Wiseman P.E., (2012), *Evaluating the potential for dendrochronological analysis of live oak (Quercus virginiana Mill.) from the urban and rural environment—An explorative study*, **Dendrochronologia**, **30**, pp. 15-21.
5. Bauch J.; Eckstein D., (1981),*Woodbiological Investigations on Panels of Rembrant Paintings,* **Wood Science and Technology**, 15, pp. 251-263.
6. Bernabei M.; Bontadi J., (2011), *Distinguishing Root- and STEM – wood of Picea Abies,* **IAWA Journal**, **32**, pp. 375-382.
7. Bernabei M.; Bontadi J.; Rognoni G.R., (2010), *A dendrochronological investigation of stringed instruments from the collection of the Cherubini Conservatory in Florence, Italy,* **Journal of Archaeological Science, 37**, pp. 192-200.
8. Bernabei M.; Pollini C., (2006), *Nota Dendrochronologica sui Tigli di S. Lugano (Bolzano, Italia),* **L'Italia Forestale e Montana, 2**, pp. 132-145.
9. Cartwright C.; Spaabek L.R.; Svoboda M., (2011), *Portrait mummies from Roman Egypt: ongoing collaborative research on wood identification,* **Technical Bulletin Research**, volume 5, The British Museum, p. 58.
10. Chaplin T.D.; Clark R.J.H.; Martinon-Torres M., (2010), *A combined Raman microscopy, XRF and SEM–EDX study of three valuable objects – A large painted leather screen and two illuminated title pages in 17th century books of ordinances of the Worshipful Company of Barbers, Lon*don, **Journal of Molecular Structure, 976**, pp. 350–359.
11. Cherubini P.; Gartner B.L.; Tognetti R.; Braker O.U.; Schoch W.; Innes J.L., (2003), *Identification, measurement and interpretation of tree rings in wooody species from mediterranean climates*, **Biology Review**, **78**, pp. 119-148.
12. Conners T., (2011), *The Basics of Wood Identification,* **Kentucky Woodlans Magazine, 6**(1), pp.4-6.

13. Cook E.R.; Kairiukstis L.A. (Ed.), (1992), **Methods of Dendrochronology: Applications in the Environmental Sciences,** Springer Science+Business Media Dordrecht, p.394.
14. Cook E.R.; Palmer J.G.; D'Arrigo R.D., (2002), *Evidence for a 'Medieval Warm Period' in a 1,100 year tree-ring reconstruction of past austral summer temperatures in New Zealand,* **Geophysical Research Letters, 29**, no. 14, pp. 1-4.
15. Cristache R. A-M., (2012), *Studii Fizio-Chimice Compleze pe o icoana din secolul XIX,* **Teza de Dizertatie,** Universitatea din Bucuresti, Facultatea de Fizica, Bucuresti, p. 120.
16. Dardes K.; Rothe A. (Ed.), (1995), **The structural Conservation of Panel Paintings Part 1: Wood Science and Technology**, The Getty Conservation Institute, Los Angeles, pp. 1-107.
17. Dardes K.; Rothe A. (Ed.), (1995), **The structural Conservation of Panel Paintings Part 2: History of Panel-Making Techniques Part 2,** The Getty Conservation Institute, Los Angeles, pp. 110-185.
18. Eckstein D.; Schweingruber F., (2009), *Dendrochronologia- A mirror for 25 years of tree-ring research and a sensor for promising topics,* **Dendrochronologia, 27**, pp. 7-13.
19. Egel E.; Simon S., (2013), *Investigatin of the Painting Materials in Zhongshan Grottoes (Shaanxi, China),* **Heritage Science, 1**, pp. 1-12.
20. Esper J.; Buntgen U.; Luterbacher J.; Krusic P.J, (2013), *Testing the hypothesis of post-volcanic missing rings in temperature sensitive dendrochronological data,* **Dendrochronologia,** p. 7.
21. Favaro M.; Guastoni A.; Marini F.; Bianchin S.; Gambirasi A., (2012), *Characterization of lapis lazuli and corresponding purified pigments for a provenance study of ultramarine pigments used in works of art,* **Analysis Bioanalogy Chemistry**, **402**, pp. 2195-2208.
22. Gartner H.; Schweingruber F.H., (2013), **Microscopic Preparation Techniques for Plant Stem Analysis**, Verlag Dr. Kessel, p. 20.
23. Grissino-Mayer H.D., (2001), *Evaluating Crossdating Accuracy: A Manual and Tutorial for the Computer Program Cofecha,* **Tree-Ring Research, 57**(2), pp. 205-221.
24. Grissino-Mayer H.D.; Sheppard P.R.; Cleaveland M.K.; Cherubini P.; Ratcliff P.; Topham J., (2009), *Adverse implications of misdating in dendrochronology: Addressing the re-dating of the ''Messiah'' violin,* **Dendrochronologia,** pp.1-11.
25. Hayashi M.; Sandu I.; Tiano P.; Maccioni N., (2009), **The Effect of Preservative Interventions on the Chemical-Physical and Structural Chracteristics of Panel Painting**, Al.I.Cuza University Publishing House, Iaşi
26. Higgitt C.; White R., (2009), **Journal of Cultural Heritage**, **10**, pp. 275–280.
27. Izzo, F.C., (2009-2010), *20th century Artists' Oil Paints: A Chemical-Physical, Survey*, **Tesi di Dottorato**, Università Ca' Foscari Venezia, Venezia, p. 226.

28. Jansma E.; Hanraets E.; Vernimmen T., (2004), *Tree-Ring Research on Dutch and Flemish Art and Furniture*, **Reihe Umwelt, 44**, pp. 139 - 146.

29. Kern Z.; Popa I., (2009), *Assessing temperature signal in X-ray densitometric data of Norwar Spruce and the earliest instrumental record from the Southern Carpathians*, **Journal of Environmental Geography**, **2,** pp. 15-22.

30. Keune, K., (2005), *Binding Medium, Pigments and Metal Soaps Characterized and Localized in Pain Cross-Section*, **PhD Thesis**, University of Amsterdam, MOLART Series, AMOLF, Amsterdam, pp. 128-132;

31. Leavengood S.A., (1998), **Identifying Common Northwest Wood Species: A Woodworker's Guide,** Oregon State University Extension Service, p. 16.

32. Macchioni N.; Lazzeri S., (2013), Tilmen Hoyuk; *Identification of wood species from areas E and G*, **Gaziantep Regional Project Occasional Paper, 4**, p. 3.

33. Macchioni N.; Lazzeri S.; Sozzi L.; Vitiello R., (2011), *Wooden sculptures from XII and XVIII centuries in the region of Asti (Italy): Scientific identification of the species*, **International Journal of Conservation Science, 2**(4), pp. 251-260.

34. Maxwell R.S.; Wixom A.J.; Hessl A.E., (2011), *A comparison of two techniques for measuring and crossdating tree rings*, **Dendrochronologia, 29**, pp. 237-243.

35. Naumann A.; Navaro-Gonzalez M.; Peddireddi S.; Kues U.; Polle A., (2005), *Fourier transform infrared microscopy and imagind: Detection of fungi in wood*, **Fungal Genetics and Biology**, **42**, pp. 829-853.

36. Nechita C., (20130), *The dendroarchaeology- review of dating the patrimony items across the globe*, **Journal of Horticulture, Forestry and Biotechnology**, **17**, pp. 34-40.

37. Norton D.A.; Ogden J., (1987*), Dendrochronology: A review with Emphasis on New Zealand Applications*, **New Zealand Journal of Ecology**, **10**, pp. 77-95.

38. Padfield J.; Saunders D.; Cupitt J.; Atkinson R., (2002), *Improvements in the Acquisition and Processing of X-ray Images of Paintings*, **National Gallery Technical Bulletin, 23**, pp. 62-75.

39. Pathan A.K.; Bond J.; Gaskin R.E., (2008*), Sample preparation for scanning electron microscopy of plant surfaces—Horses for courses*, **Micron**, **39**, pp, 1049-1061.

40. Patrut A.; Von Reden K.F.; Lowy D.A.; Patrut R.T.; Vaida D.L.; Margineanu D., (2013), *Old ages of two historical Romanian trees assessed by AMS radiocarbon dating*, **Nuclear Instruments and Methods in Physics Reasearch B**, **294**, pp. 616-621.

41. Pichler T.; Nicolussi K.; Goldenberg G., (2009), **Dendrochronological analysis and dating of wooden artefacts from the prehistoric coppermine Kelchalm/Kitzbuhel (Austria), Dendrochronologia, 27**, pp. 87-94.