

CHARACTERIZATION OF HISTORICAL VIOLIN VARNISHES USING ATR-FTIR SPECTROSCOPY

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Abstract. Traditional, historical varnishing techniques applied on ancient musical instruments have been increasingly studied within the last decades, a comprehensive physico-chemical characterization of these coatings being important not only for art historical analysis of artifacts but for proper restoration and conservation treatments as well. In this paper we discuss the chemical composition and micro-structure of materials used in violin varnishes, with a case study focused on a copy of 1712 Antonio Stradivari violin made in 1963 by Romanian master luthiers in Reghin. Defined as a clear, protective layer of organic film-making substances coated onto the surface, musical instrument varnishes are in general various mixtures of natural products – drying oils, essential oils, tree resins, gums, etc. – that may be difficult to analyze due their complex composition and natural variability. The results obtained in our study, on micro-samples without any special pre-treatment, by the use of Fourier Transform Infrared – Attenuated Total Reflectance (FTIR-ATR) Spectroscopy, highlights characteristic absorption bands that indicate the presence of triterpenic resins (possible Dammar) and siccative oils. Additional data on regard the varnish layers and the ground coating are discussed *via* Scanning Electron Microscopy coupled with X-Ray Analysis (SEM-EDX).

Key words: historical musical instruments, varnish techniques, natural resins, ATR-FTIR spectroscopy, SEM-EDX.

1. INTRODUCTION

Among the earliest documentary information on regard the use of oil varnishes and resins with respect the surface finishing of works of art, recipes involving oleoresins, linseed oil, various glues or gums, treated with lime or litharge, can be found mentioned beginning with the 9th century [1]. Due to their heterogeneous and transitory nature, and nevertheless the introduction of synthetic resins into the 20th century art market, an exact insight into the history of surface coating materials has its inherent complexities, starting with its general description – as from a structural chemical aspect historical varnishes are significantly

different than the ones used today [1–2]. In the case of wooden musical instruments, especially stringed ones, the practice of varnish techniques has had its golden age within the mid-16th century Italian lutes, the varnish recipes of this period being considered to have not only a protective and aesthetical role, but an acoustical one as well [3] with sound quality as a result of both the construction technique and combination of materials used [4]. Taking into consideration the scientific studies [5–8] carried within the latest decades on the characteristics of coatings materials applied on historical musical instruments' surfaces, classical varnishes appear in most of the analyzed cases as complex mixtures of organic layers, occasionally blended with inorganic compounds that interact, age and degrade in a strong heterogeneous matrix [9]. In order to improve the diagnostic research – stratigraphic and micro-chemical analysis of the layers, morphology of the interfaces, functional or molecular composition of organic products, mineral composition and particles distribution in the binder, etc, and nevertheless their statistical relevance [3–4] while still preserving the integrity of the instrument when studying authentic original artworks, a non-invasive approach is required – with test copies reproducing the presumed materials used within the original instrument [4]. In the context of a combined analytical methodology that could provide extensive information on the above mentioned areas of interest, Attenuated Total Reflectance (ATR) Fourier Transform Infrared Spectroscopy and its derivative techniques [6], can be considered as a powerful method when analyzing and mapping organic species of heterogeneous stratigraphic materials [10]. Focused on a 1712 Stradivari violin copy manufactured during 1963 in Reghin (Romania), the present paper is intended to be an analytical and technical study of wooden musical instrument varnishes as well as an insight into the potential of IR spectroscopic techniques as a discrimination tool when dealing with complex organic materials.

2. MATERIAL AND METHODS

The object of this work deals with the varnish of a violin instrument manufactured in the early 1960s in Reghin after an 18th century Stradivari model; belonging to Victor Brauner School of Fine Arts (Piatra Neamt, Romania) the violin was played until 2003, when after an incident the arm and sound cavity were fractured. For the study, a number of three micro-samples were collected with the use of a scalpel from areas that showed no evidence of retouching or repairs. Optical microscopy analysis was performed with the use of a Carl Zeiss Axio Imager A1m having an Axiocam camera attached. Images at variable magnification were captured. For morphological and elemental mapping SEM investigations were carried *via* a Tescan Vega LSH scanning electron microscope coupled with a Quantax QX2 X-ray spectrometer. Secondary electron images were

taken at an operating voltage of 30 kV; samples were gold coated. Further, for molecular characterization ATR-FTIR analysis was performed using a PerkinElmer Spectrum Two FTIR spectrometer, equipped with a PIKE Technologies ATR accessory with a monolithic diamond crystal. Spectra were collected in the mid infrared range $4,000\text{--}450\text{ cm}^{-1}$ at a spectral resolution of 4 cm^{-1} by averaging 16 scans, with automatic background subtraction; no special sampling preparation was required. Multiple measurements were carried both on micro-samples as well as *in situ*, by direct contact of the artwork with the crystal surface. Excellent technique when studying thin surface layers, its applications sets certain care as damage of fragile materials can occur due to the high pressure exerted by the ATR crystal on the analyzed sample; the relative positioning of the specimen in relation with the ATR crystal is also particularly important as the achieved optical contact is directly related with the data quality obtained [6]. Taking into consideration these technical aspects for *in situ* measurements minimum pressure was applied, while in the case of varnish micro-samples spectra were recorded under higher force. In terms of data processing, all spectral data presented here was baseline corrected and a smooth factor applied.

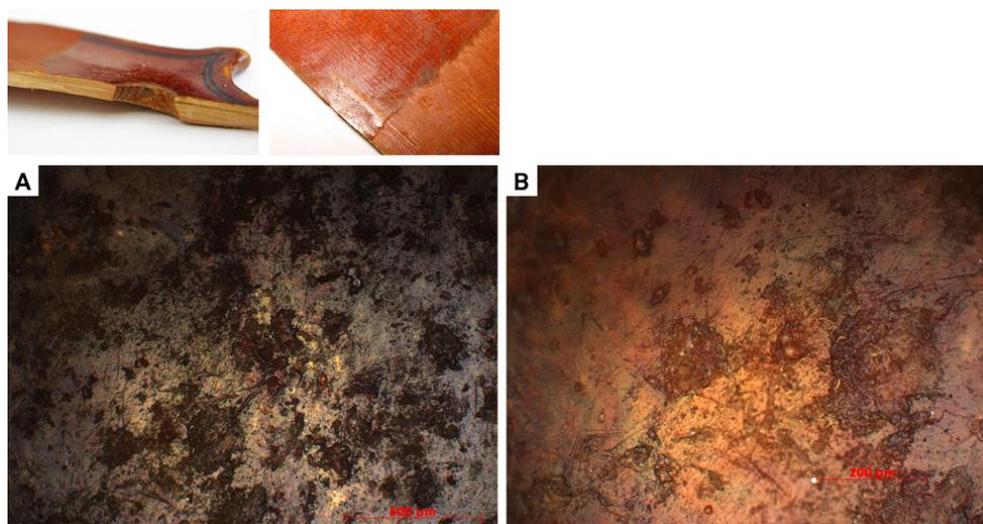


Fig. 1 – Violin fragment, back plate, with details under optical microscope examination (A – $100\times$ / B – $200\times$); due to aging factors, environmental and inadequate storage conditions the varnish film is visibly degraded and quite extensive areas can be characterized by a gloss loss, a mat finish with visible scratches, craquelure and exfoliations, and a general poor adherence onto the wood substrate; at higher magnifications crystalline particles can be clearly observed apparently concentrated in the lower part, above the wood surface.

3. RESULTS AND DISCUSSIONS

IR spectra provided characterization of the major molecular and chemical components in the analyzed varnish samples, the identified chemical functional groups pointing to an oil varnish recipe based on triterpenic resins mixed with siccative oils. According to previous literature [11–13] specific absorption bands for triterpenic resins molecules were recorded within the range of $3079\text{--}2650\text{ cm}^{-1}$ $\nu(\text{C-H})$, $1713\text{--}1706\text{ cm}^{-1}$ $\nu(\text{C=O})$, 1650 cm^{-1} (vinyl), 1450 cm^{-1} $\delta(\text{CH}_3)/\delta(\text{CH}_2)$, 1315 cm^{-1} , $1230\text{--}1270\text{ cm}^{-1}$, $\nu(\text{C=C})$ and $1037\text{--}1035\text{ cm}^{-1}$ $\nu(\text{C-O-C})$, along a series of IR absorption bands in the fingerprint region that may be attributed to the presence of a drying oil (specific peaks within this region at 1044 cm^{-1} , 720 cm^{-1}) and possible mineral fillers or impurities (Fig. 2). As a general pattern within all micro-samples examined, slightly deviations were observed for the main characteristic absorption bands in relation to those found in literature, as well as certain band distortions that may be due either to the heterogeneous nature of the analyzed materials, with band overlapping, or to the ATR acquisition mode and its specific experimental factors that may affect the final spectrum [14] as the observed absorbance depends not only on the area of material in direct contact with the crystal surface but on the distribution of the sample within the evanescent field as well.

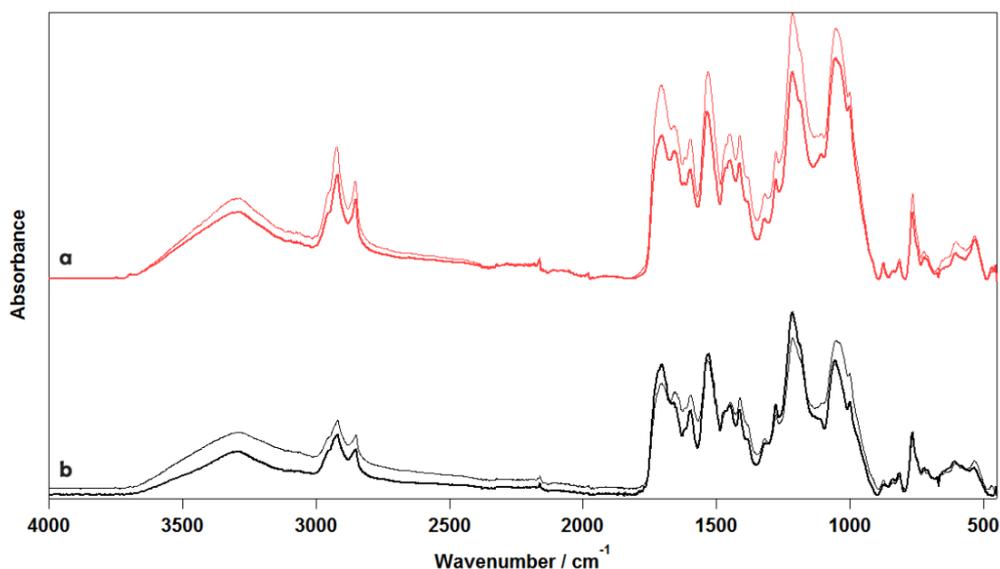


Fig. 2 – ATR-FTIR spectra obtained on analyzed varnish micro-samples (a) compared to *in situ* measurements (b); good correlation in respect to specific IR absorption bands can be seen, with only minor variations in band intensities due to experimental factors – such as applied force, quality of the achieved optical contact, depth of penetration, etc., and/or local material characteristics.

Taking into consideration the overall weaker resin signal when compared to a fresh varnish [11], we assume the existence within the analyzed samples of various levels of degradation that generates IR results mixing molecular fingerprint of both fresh as aged resins. Under these aspects, the global decrease of the C-H band around 2919, 2853 cm^{-1} and of the C=C absorption band at 1650 cm^{-1} , and on the other hand the increased absorbance observed in the 3200–3400 cm^{-1} region, could be explained by undergoing natural ageing process, with autoxidation and crosslinking reactions affecting the polymeric fraction. Moreover, with interactions and/or ageing products that may be present within the matrix [15–16], an exact attribution of absorption bands has clear limitations, recent studies [11] on regard molecular characterization of aged mixtures of natural resins and oils suggesting that the identification by specific absorption bands is only possible in unknown sample by determination of the resin type via combination of specific and non-specific band, with no precise identification possible in the case of triterpenic resins that exceeded a certain degradation stage without advanced multivariate analysis [11, 17].

In terms of the oil medium, the shifting and broadening of the carbonyl band due, as previous stated [18], to the formation of carboxylic acids – as one of the most pronounced effects observed in the infrared spectra of oil-based varnishes and paints, affects significantly the identification of characteristic peaks that may discriminate between the various drying oils that may have been used within the varnish formulation (linseed oil, walnut oil, castor oil), as the relative proportion of saturated and unsaturated fatty acids can be considered the only major factor that differentiates these oils [19].

On another approach focused on morphological and elemental characterisation, SEM/EDX analysis allowed the identification of a series of inorganic substances present within the varnish layer, among the major components being found silicon, aluminum, sodium and magnesium, followed in smaller amounts by sulfur, calcium, potassium and chlorine, trace elements that may point towards various inorganic compounds that may have been added as fillers [5] – quartz or glass, potassium feldspar, gypsum, clay or other calcium sulphates; or may be present as impurities either as part of the original materials or embedded later, via contamination of the varnish film. For the elemental distribution within the analysed samples some aspects need though to be clarified as the investigations were carried through the varnish layer and thus absorption of elements in the uppermost layers may be disproportionally over-represented in the spectra, in contrast to those found in deeper regions due to soft X-rays attenuation [20]. With this aspects taken into account we can only assume based on the occurrence of detected elements and FTIR results, the presence of manganese based earths added as a pigment along with a series of inorganic fillers diffused within the matrix, while the identified trace elements can be explained as contaminants assigned to human sweat [21] or, to a lesser extent, to the inorganic portion of wood below the

varnish, calcium and potassium being among the most abundant inorganic elements found in wood species.

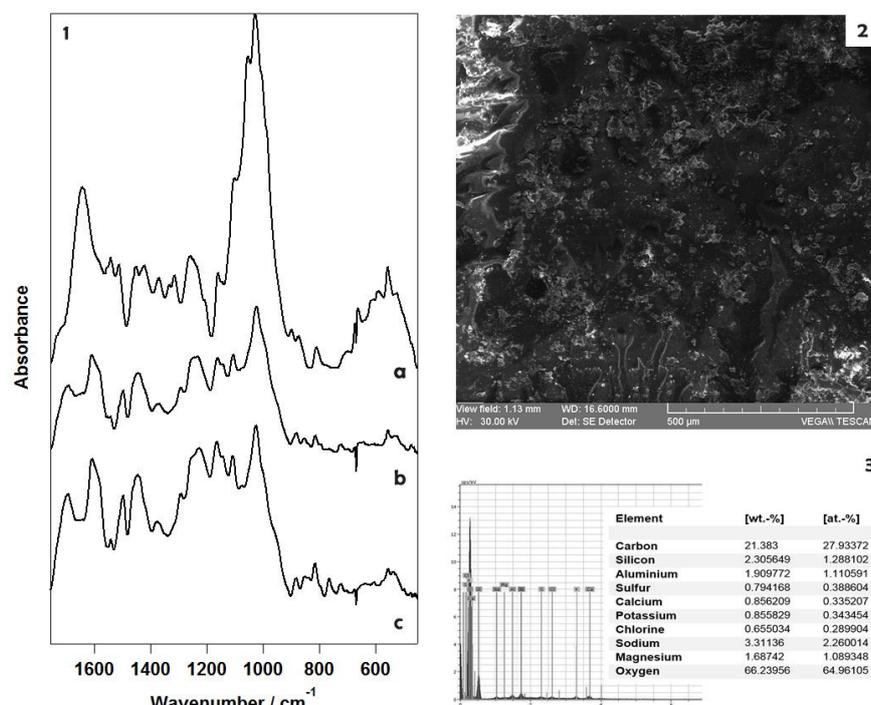


Fig. 3 – FTIR results (1) on wood – clean, back area of the analyzed violin fragment (a), compared to impregnated wood (b) (top of the fragment, varnish exfoliated area), and back side of a varnish micro-sample (c); SEM image (2) revealing the heterogeneous nature of the coating characterized near the surface by an amorphous fracture and a high concentration of solid particles dispersed within an insoluble dense organic binder; EDX spectrum (3) and recorded microanalysis data (K series).

The presence of an intermediate mineral interface between wood substrate and varnish layer, or the wood treatment prior to varnishing with special aqueous solutions, are also possible situations if we analyse FTIR data (Fig. 3) obtained on clean wood, varnish exfoliated areas and back top of a varnish micro-sample, where, in the last two cases, the fingerprint region follows a similar pattern, but not when compared to previous IR varnish spectra (Fig. 2), fact that may suggest the presence of several layers with various composition and/or densities. For conclusive information on regard materials distribution and ultimately on the varnish technique, investigations carried on cross sections with elemental and molecular area map would be required.

4. CONCLUSIONS

ATR-FTIR investigations combined with SEM-EDX analysis allowed an insight into the molecular, morphological and elemental characteristics of the varnish applied on the violin surface, with a traditional varnish-oil recipe identified based on triterpenic vegetal resins mixed with siccative oils, along a series of inorganic fillers and earth pigments added to the formulation. IR analysis highlighted the presence of carboxylic acids with oxidation and cross-linking as possible reactions occurring within the matrix that generates certain distortions on regard characteristic absorption bands that significantly hinders an exact band attribution. With only subtle differences generated by the presence of one or more specific compounds or their relative amounts, the positive identification of a specific resin tends to be extremely difficult and for better peak-to-peak comparison of sample spectra to library ones, and thus better molecular characterization of the resin type, chemometric models based on principal component analysis are needed. Moreover, in correlation with recorded SEM-EDX investigations that point an overall heterogeneous matrix and a poor surface conservation of the film coating that appears to be affected at both mechanical and chemical level, aging process are shown to be more dynamic and extensive within varnishes that generally believed.

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