Spectroscopic Analysis to Characterize Finishing Treatments of Ancient Bowed String Instruments

The art of violin making: rediscovering the ancient Cremonese finishing treatments through non-invasive and micro-destructive techniques

Giacomo Fiocco [1], Tommaso Rovetta [1], Monica Gulmini [2], Anna Piccirillo [3], Maurizio Licchelli [1,4], Marco Malagodi* [1,5]

[1] Laboratorio Arvedi di Diagnostica Non-Invasiva, Università di Pavia, Via Bell'Aspa 3, 26100 Cremona, Italy

[2] Dipartimento di Chimica, Università di Torino, Via Giuria, 7, 10125 Torino, Italy

[3] Centro Conservazione e Restauro "La Venaria Reale", Via XX Settembre 18, 10078 Venaria Reale (TO), Italy

[4] Dipartimento di Chimica, Università di Pavia, Via Taramelli 12, 27100 Pavia, Italy

[5] Dipartimento di Musicologia e Beni Culturali, Università di Pavia, Corso Garibaldi 178, 26100 Cremona, Italy

MM*: marco.malagodi@unipv.it; +39 3496445217

***corresponding author**

Keywords

MUSICAL INSTRUMENT, VARNISH, WOOD TREATMENT, XRF, SEM-EDX, FTIR

Acknowledgments

We would like to thank the International violin-making school of Cremona and M° Alessandro Voltini in particular, for providing the fragments of the historical musical instruments. A special thanks to Elisa Scrollavezza and Andrea Zanrè for the handwritten notes of the Masters Gaetano and Pietro Sgarabotto.

Abstract

Historical bowed string instruments exhibit acoustic features and aesthetic appeal that are still considered inimitable. These characteristics seem to be in large part determined by the materials used in the grounding and varnishing treatments after the assembly of the instrument. These finishing processes were kept secret by the violin makers, and the traditional methods handed down orally from masters craftsmen to apprentices. Nowadays, the methods of the past can represent a secret to be revealed through scientific investigations, since the "Cremonese" methods used in the 17th and 18th century were lost as the last great Masters from the Amati, Guarneri and Stradivari families passed away. In this study, we had the chance of combining non-invasive and micro-invasive techniques on six fragments of historical musical instruments. The fragments were detached from different instruments during extraordinary maintenance and restoration treatments, which involved the substitution of severely damaged structural parts like top plates, back plates or ribs. Therefore, the fragments can offer to the

scientists a valuable overview on the materials and techniques used by the violin makers. The results obtained by portable X-ray fluorescence, optical microscopy, scanning electron microscopy coupled with energy dispersive X-ray spectrometry, and Fourier transformed infrared microscopy led us to: (i) determine the stratigraphy of six instruments; (ii) obtain new information about the materials involved in the finishing processes employed in Cremona; (iii) elucidate the technological links among the procedures adopted in the violin making workshops during the considered period.

1. Introduction

Wooden musical instruments are normally protected from moisture, dust and biological agents by a single or multi-layered coating applied as a finishing treatment on the wood [1]. All the layers actively contribute to enhance the aesthetic quality of the wood textures and also play a role in determining the acoustic features of the instrument [2, 3]. Bowed string instruments produced in Cremona (Italy) during the 17th and 18th centuries, when the most important violin-makers were active, are still considered inimitable both for the construction techniques and the materials used. The interest in knowing which construction procedures were employed is thus greatly stimulated. Few tangible records give scarce information about the original recipes of the old Masters and the general lack of robust information led some authors to propose empirical procedures to reproduce the ancient varnishes [4-7]. More recently, analytical tests performed by physical and chemical techniques have led to characterize some of the materials that can be encountered in the complex stratigraphy of the finishing layers. The materials adopted in the finishing process had prevalently an organic nature, being mainly represented by siccative oils, animal glues, vegetable gums, gum-resins, resins, waxes and natural dyes [8]. In addition, some inorganic components were identified in finishing materials, in order to impart specific properties such as the colour, to enhance the siccative nature of the mixture or to act as fillers of the wood porous [8, 9-11].

However, samples for analytical purposes are normally not available from such valuable instruments and non-invasive analytical approaches are necessary; this condition makes difficult to obtain information on the varnish stratigraphy. When sampling is feasible, scientific strategies allowing subsequent observations by different analytical techniques on a same sample shall be selected. Because of the complex nature of the multi-layered stratigraphy, the in-depth characterization of each layer can be performed only by combining a set of analytical techniques. Besides the preliminary optical inspection under high magnification with visible and UV lights, elemental and molecular spectroscopic techniques, diffractometric investigations and chromatographic techniques have been employed synergistically [8, 12-18].

In this work, we had the exceptional opportunity of combining non-invasive and micro-destructive analytical procedures on six fragments previously removed from Cremonese historical instruments. The set of the considered fragments represents a valuable record of the methods employed by the violin makers in Cremona during the 17th and 18th century. A preliminary non-invasive approach has been developed using visible and ultraviolet photography, stereoscopic microscopy, radiography and X-Ray Fluorescence (XRF). The micro-invasive approach has been carried out after a selective sampling on the

fragments, in order to highlight the stratigraphy and to perform micro-analysis on each layer. Optical microscopy, electron microscopy coupled with energy dispersive X-Ray spectroscopy (SEM-EDX) and micro Fourier Transform Infrared Spectroscopy (μFTIR) have been used for imaging the samples in order to investigate their microstructure, and for identifying the various materials in the finishing layers.

The aim of the investigation is to obtain information about the materials and construction methods of the old Masters. Moreover, such a peculiar set of samples also enable us to investigate the technical relations among the different workshops, highlighting the links between Masters and apprentices - if any - or the specificity of each violin maker's procedures.

1.1. The Sgarabotto collection

The fragments considered in this study are shown in Fig. 1. They are a part of a larger collection donated in 1983 from the violin maker Pietro Sgarabotto (1903-1990) to the International Violin Making School of Cremona. During the first half of the 20th century, Pietro Sgarabotto, and mostly his father Gaetano (1878-1959), restored several stringed historical instruments by substituting the heavily damaged parts (i.e. top plates, back plates or ribs). The original fragments were kept as models by the two violin makers, in order to imitate the varnish appearance in the construction of their modern instruments [19]. The six fragments were selected on the basis of their chronological attribution (i.e. between 1650 and 1750), in order to represent the Cremonese school during the "Golden Age" of the violin making art. At that time, bowed string instruments from Cremona reached the highest quality thanks to the work of great masters such as Amati, Stradivari, Guarneri and Guadagnini [20]. The fragments removed by Gaetano and Pietro Sgarabotto were marked with a handwritten inscription on the verso side, which indicates the violin maker that produced the original instruments. Moreover, they took some notes during their restorations, and these written documents further support the attribution. Table 1 reports some details on the considered fragments.

The selected set of fragments also offers the opportunity of investigating the possible links between the Master craftsmen and their apprentices, since Nicola Amati (1596-1684), probably the most influential luthier of the 17th century, was the master of Jacobus Stainer (1617-1683), Andrea Guarneri (1626-1698) and Francesco Ruggeri known as "il Per" (1630-1700). Antonio Stradivari (1644-1737) also learned the art of violin making in the Amati's workshop and he was in turn probably the master of Lorenzo Guadagnini (1685-1746). Guadagnini was in fact mainly active in Piacenza and Milan, although he learned in Cremona the art of violin making [20].

2. Instruments and methods

The characterization of the materials in the finishing layers was carried out through a multi-analytical approach combining non-invasive and micro-destructive techniques. A preliminary observation was performed through a Nikon D4 full-frame digital camera (Minato, Tokyo, Japan) equipped with a 50mm f.1.4 Nikkor objective. Visible light illumination was obtained

by a Softbox LED lamp (30s exposure time, f.11, ISO 400), while UV-induced visible fluorescence was obtained through two Philips TL-D 36W BBL IPP low-pressure Hg tubes (emission peak at ~365 nm). UV illumination was employed to detect any non-original material on the surface, in order to select the areas of analytical interest for the subsequent analyses. Details were observed through a stereomicroscope Olympus SZX10 (Shinjuku, Tokyo, Japan) equipped with an Olympus DP73 camera and a Schott KL1500 illuminator. XRF was carried out on the fragments using an ELIO portable X-Ray Fluorescence Spectrometer produced by XGLab (Milan, Italy). The X-ray source worked with a Rh anode and a spot diameter of 1.3mm. XRF spectra were collected on 2048 acquisition channels by fixing the tube voltage at 40 kV, the current at 80 μA and the measuring time of 180s. Data were processed using the ELIO 1.5.5 software.

Some micro-samples, bearing the characteristic of the whole stratigraphy, were collected using a scalpel. Cross-sections were obtained by embedding the samples into epoxy resin (Epofix Struers and Epofix Hardener with ratio 15:2) and by polishing them with silicon carbide fine sandpaper (800-4000 mesh). The polished cross-sections were thus observed through a polarized light optical microscope Olympus BX51TF equipped with an Olympus TH4-200 lamp (visible light) and an Olympus U-RFL-T (UV radiation). Imaging at higher magnifications and micro-analyses were performed by SEM-EDX using a FE-SEM Tescan Mira 3XMU-series (Brno, Czech Republic), set with an accelerating voltage of 15-20 kV in high vacuum and equipped with a Bruker Quantax 200 Energy-Dispersive X-ray spectrometer (Billerica, Massachusetts, USA). Before the SEM-EDX investigation, the samples were made conductive with a graphite coating obtained by a Cressington Carbon Coater 208C. Data were then processed using the Bruker Esprit 2 microanalysis software.

Further micrometre-sized samples were detached directly from each layer by a scalpel; the collected materials were pressed and flattened by means of a diamond cell to ideal thickness for μFTIR. They were then analysed in transmission mode with a Bruker Vertex 70, equipped with a Bruker Hyperion 3000 infrared microscope. Data were processed by the EZ Omnic 7.3 software.

3. Results

3.1. Fragment from a viol by Nicola Amati

The stratigraphy of the Amati fragment shows one varnish layer applied directly on the maple wood substrate. Preliminary non-invasive XRF analyses highlighted high signals of K, Ca and Fe and lower of S, Ti, Mn, Cu and Zn. The observation of the cross-section under the optical and the electron microscope (Fig. 2a,b) allows us to identify a deformation of the wood structure (Fig. 2a,b, layer W) under the varnish, suggesting the application of a chemical treatment to seal the porosity of the wood. This was partially confirmed by UV-induced fluorescence that revealed a yellow-brown fluorescence along the treated upper tracheids (first 20 μm of the wood), evidence of the application of a surface treatment which has altered the wood structure. EDX analyses performed on the wood reveal the emission peaks of Na, Mg, Si, S, Cl, K and Ca. This elemental composition, especially the high counts of Na and K, in addition to the altered structure of the tracheids, seems to confirm a

chemical pre-treatment of the wood [21, 22]. The study of the cross section could evidence as the varnish layer (Fig. 2, layer V) has been applied directly on the substrate, without any preparation layer applied. The varnish shows a characteristic white UV fluorescence and a thickness of 10 µm. EDX analyses performed on the varnish highlight only weak peaks of Na, Mg, S, Cl, K and Ca. The nature of the varnish was disclosed by µFTIR analyses (spectrum not reported), which revealed the presence of a natural resin probably mixed with a siccative oil (νC-H_2 at 2928 cm^{-1} and 2855 cm^{-1}; νC=O at 1730 cm^{-1} and 1716 cm^{-1}; δC-H at 1457 cm^{-1}; νC-O at 1239 cm^{-1} and 1162 cm^{-1}). Signals of gypsum (νO-H 3528 and 3403 cm^{-1}; νS-O_4 1141 and 672 cm^{-1}), oxalates (νC=O at 1652 cm^{-1}; νC-O_2 at 1322 cm^{-1}) and silicates (νSi-O at 1194 cm^{-1} and 1056 cm^{-1}) have been also identified in the varnish [23]. The presence of silicates could be attributed to some residues of the chemical treatment applied on the wood [6].

3.2. Fragments from two cellos (A and B) by Jacobus Stainer

The first fragment attributed to a cello by Stainer is henceforth indicated as Stainer A. It shows a stratigraphy with two superimposed layers applied on the maple wood substrate. XRF analyses could highlighted high signals of K, Ca and Fe were found, as well as lower signals of S, Mn, and Cu. Higher amounts of Zn and Pb have been detected in three analytical spots. Optical and electron scanning microscopy (Fig. 3a) performed on the cross-section showed in this case a well-preserved structure of the tracheids (Fig. 3a, layer W), confirmed by EDX analyses that did not highlight evidence of some wood treatment. The layer superimposed on the wood (Fig. 3a, layer P) had a homogeneous thickness of 20 µm and it was characterized by a light-blue UV induced fluorescence. The µFTIR analyses, carried out on a micro-sample collected from this layer, was characterized by signals of C-H and N-H (νN-H at 3276 cm^{-1}; νC-H 3079 cm^{-1}), of the primary amide (νC=O at 1645 cm^{-1}) and of the secondary amide (νC-N and δN-H at 1547 cm^{-1}). These bands could be ascribable to the presence of a proteinaceous materials used as ground coating. Weak bands of carbonates (νC-O at 1422 cm^{-1}; δC-O_2 at 872 cm^{-1}) were detected, indicating the possible presence of calcite. EDX spectra obtained from this layer showed weak emission peaks of Na, Si, P, K and Ca; however no evidence of inorganic particles could be noticed. The upper varnish layer (Fig. 3a, layer V) has a thickness of 15 µm and shows a yellowish UV induced fluorescence. The µFTIR analysis performed on this layer showed intense bands characteristics of the aliphatic chains (νC-H_2 at 2927 and 2855 cm^{-1}; δC-H at 1461 cm^{-1}) and carbonyl and carbon-oxygen bond (νC=O at 1711 cm^{-1}; νC-O at 1250 and 1162 cm^{-1}), which could be ascribable to a natural resin. µFTIR characteristics signals of oxalates (νC=O at 1647 cm^{-1}; νC-O_2 at 1321 cm^{-1}) [23], in addition to those of residues of the underneath proteinaceous material, have also been identified. EDX analysis (Fig. 3b) carried out on a micrometric particle dispersed in this upper layer reveals the characteristic emission peaks of Mg, Al, Si, S, Cl, K, Ca and Fe: this elemental composition could be ascribable to silicates, feldspars and iron oxides/hydroxides, related to the presence of clay and inorganic pigment such as ochre [24].

The second fragments from another cello by Steiner is henceforth indicated as Steiner B. As reported in Fig. 3c, it shows features that resemble those observed in the fragment Stainer-A, with two layers on the wood. XRF spectra collected from selected spots on the surface revealed the characteristic emission peaks of S, K, Ca, Ti, Mn, Fe, Cu and Zn. Low signals of Ni and Pb have been incidentally detected in one analytical spot. Under the optical microscope with UV illumination, the cross section showed a well preserved structure of the wood tracheids (Fig. 3c, layer W) and a ground layer (10 µm thick) with a light-blue UV fluorescence (Fig. 3c, layer P). The µFTIR analyses highlighted the presence of proteinaceous materials (νN-H at 3329 cm^{-1}; amide I νC=O at 1651 cm^{-1}; amide II νC-N and δN-H at 1546 cm^{-1}; amide III δC-H at 1451 cm^{-1}), carbonates (νC-O at 1416 cm^{-1}; δC-O at 877 cm^{-1}) and oxalates as alteration products. Furthermore, EDX spectra show signals from N, Na, Mg, K and Ca. The upper layer (Fig. 3c, layer V) has a uniform thickness of 20 µm and a characteristic orange-yellowish UV fluorescence with fine cracks and some dark inclusions. µFTIR analyses (Fig. 3d) confirmed the presence of a natural resin (νC-H_2 at 2928 cm^{-1} and 2857 cm^{-1}; νC=O at 1711 cm^{-1}; δC-H_2 at 1461 cm^{-1}; νC-O at 1251 cm^{-1} and 1169 cm^{-1}) and traces of oxalates (νC=O at 1645 cm^{-1}; νC-O_2 at 1319 cm^{-1}). EDX analysis revealed the presence of Na, Al, Si, K e Ca attributable to a mix of inorganic components (quartz and feldspars) dispersed in the varnish [24].

3.3. Fragment from a cello by Andrea Guarneri

The fragment attributed to Andrea Guarneri has the most complex stratigraphic structure, with three different layers applied on the wood. XRF analyses performed on the surface of the fragment revealed high counts of K, Ca and Fe with minor of S, Ti, Cr, Mn and Zn. By observing the cross-section with the optical microscope (Fig. 4a), no deformation of the upper tracheids of the substrate (Fig. 4a,b, layer W) could be noticed. EDX analysis carried out on the wood under the ground layer, showed weak signals of Na, K and Ca, characteristic of an untreated spruce wood [25]. A grey-violet/blue fluorescence was detected on the ground coating (Fig. 4a,b, layer P) under UV illumination. White particles were identified as gypsum both by SEM-EDX (Fig. 5b,c) and by µFTIR analyses. Besides the bands of gypsum (νO-H 3519 cm^{-1} and 3400 cm^{-1}; νS-O_4 1113 cm^{-1} and 672 cm^{-1}), the µFTIR spectra of this layer also reveal the presence of proteinaceous materials (νN-H at 3282 cm^{-1}; amide I νC=O at 1646 cm^{-1}; amide II νC-N and δN-H at 1552 cm^{-1}) and oxalates (νC=O at 1647 cm^{-1}; νC-O_2 at 1320 cm^{-1}). Upon the ground layer, a dark red-violet coloured layer (Fig. 4a,b, layer CL) with a thickness of 10 µm and a faint red-purple UV fluorescence is observed. EDX analysis revealed the presence of Na, Mg, Al, Si, S, K, Ca and Fe, with low signals of P. This composition might suggest the presence of silicates, feldspars and iron oxides/hydroxides, probably associated to an intentional use of red ochres [26]. The external varnish layer (Fig. 4a,b, layer V) has a uniform thickness of 20 µm and a bright white UV fluorescence. The µFTIR analysis carried out on a micro-sample from this layer reveals signals that could be related to various natural resins. The possible presence of diterpenic resins (i.e. sandarac, copal) is suggested by some characteristic bands (νC-H at 3083 cm^{-1}; νC-H_2 at 2930 cm^{-1} and 2857 cm^{-1}; νC=O a t 1710 cm^{-1}; νC=C at 1641 cm^{-1}; δC-H at

1460 cm^{-1}, νC-O at 1251 cm^{-1}) [23], which have been identified in addition to weak signals of oxalates (νC=O at 1641 cm^{-1}; νC-O_2 at 1320 cm^{-1}).

3.4. Fragment from a cello by Francesco Ruggeri known as "il Per"

The stratigraphy of the Ruggeri fragment shows two superimposed layers applied on a maple wood substrate (Fig. 5). XRF analyses carried out on the surface of the fragment revealed the emission peaks of S, K, Ca, Ti, Mn, Fe, Cu, Zn, Pb and traces of Sr. EDX analysis carried out on the wood structure (Fig. 5a, layer W) revealed the presence of weak signals of Si, S, Cl, K and Ca, which are characteristic of an untreated wood [25]. A characteristic light-blue UV-induced fluorescence on the ground layer has been documented (Fig. 5a, layer P). The μFTIR analysis highlighted the presence of proteinaceous materials (Fig. 5b), with signals of primary amides (νC=O at 1648 cm^{-1}), secondary amides (νN-H at 3325 cm^{-1}; νC-N and δN-H 1544 cm^{-1}) and tertiary amides (δC-H at 1452 cm^{-1}). EDX analyses performed selectively on the proteinaceous ground revealed the presence of S and Ca, ascribable to gypsum, and those of Na, Mg, Al, Si, K, Ca and Fe, probably associated to the presence of silicates, aluminosilicates and iron oxides/hydroxides [26]. The external varnish layer (Fig. 5a,c, layer V), with thickness of about 20 μm, shows an orange UV-induced fluorescence; in addition, some dark particles were identified by EDX analyses (Fig. 5d) and signals of Na, Mg, Al, Si, S, Cl, K, Ca and Fe were detected. The peaks of Al, Si and Fe may suggest, also in this layer, the presence of silicates, aluminosilicates and iron oxides/hydroxides ascribable to the presence of micrometric inorganic red ochre particles.

3.5. Fragment from a double-bass by Lorenzo Guadagnini

The study of the stratigraphy has revealed two superimposed layers applied on a spruce wood substrate. The elements S, K, Ca, Ti, Mn, Fe, Cu and Zn were identified by XRF analysis performed on the fragment surface. Weak signals of Cr, Ni and Pb have been also detected. Observations of the cross-section under both optical and electron microscopes (Fig. 6a,b) show a deformation of the wood structures (Fig. 6a,b, layer W), with collapsed tracheids in the first micrometres of the wood under the ground layer. The deformation of the wood structure may due probably to a mechanical treatment necessary to smooth the rough surface, because either the EDX signals detected on the wood or the UV fluorescence (Fig. 6a) would suggest here the use of a chemical treatment. A layer of 10 μm upon the wood substrate (Fig. 6a,b, layer P) shows a brown-red UV fluorescence. EDX analyses, carried out on some particles found in this layer, revealed the presence of S and Ca attributable to gypsum, and rare small-sized particles of silicates and iron oxides/hydroxides (Na, Mg, Al, Si, P, S, Cl, K, Ca and Fe) dispersed in an organic binder. The external varnish layer (Fig. 6 a,b, layer V) shows a whitish UV fluorescence and an homogeneous thickness of 50 μm. The μFTIR analyses (Fig. 6c) performed on a micro-sample taken from this layer reveal the probable presence of a colourless natural diterpenic resin (i.e. sandarac, copal) as suggested by the following bands: νC-

H_2 at 3081 cm^{-1}, 2933 cm^{-1} and 2859 cm^{-1}; νC=O at 1710 cm^{-1}; νC=C at 1646 cm^{-1}; δC-H at 1459 cm^{-1} and 1380 cm^{-1}; νC-O at 1250 cm^{-1} and 1167 cm^{-1}

4. Discussion

The overall data obtained from the six fragments are synthetically reported in Table 2. The results of the present research confirmed some hypothesis about the construction techniques used by the baroques violin makers and they were able to ascertain in some cases the chemical composition of Cremonese materials. To gain further insights, several historical approaches were referenced, either browsing old texts for material knowledge related to violins, or integrating the scientific results of the mainly researches performed on those kind of materials.

First of all, different approaches in finishing the wood surfaces before spreading the varnish have been highlighted. The stratigraphy of the finishing layers in the Amati's fragment confirms the same sequence proposed by Barlow and Woodhouse, who investigated by scanning electron microscopy a fragment of a violin produced by the same violin maker [9]. In fact, even in this case a thin layer of varnish was applied directly on the treated wood without any proteinaceous ground layer. Moreover, Brandmair and Greiner documented the stratigraphy collected on the violin "Alard" made by Nicola Amati in 1649 [27], and they highlighted a similar varnish layer spread directly onto the wood, supporting the hypothesis that this treatment may be considered as characteristic of the Amati's production. Those results support the ideas that a chemical treatment was applied on the rough wood before the application of the subsequent layers, generally different coatings of organic substances such as oil, resin, glue, wax, gum, or protein. Additional hypothesis about Cremonese wood treatment have been reviewed by Sacconi [6], who supposed the presence of a silicates-based chemical treatment applied on the wood of the Stradivari's masterpieces.

However, on the basis of our results, a second group of fragments showed a different procedure: a proteinaceous coating spread over the untreated wood has been identified in the four coeval fragments attributed to Stainer, Ruggeri and Guarneri, all apprentices in the workshop of Nicola Amati. This wood preparation was supposed by Bachmann [28] who identified the presence of a glue-based ground layer applied between the wood and the external varnish layers on the historical instruments made in Cremona during the 17^{th} and 18^{th} century. This ground layer embeds different inorganic fraction mainly composed of carbonates (Stainer A and B), calcium sulphates (Guarneri) and calcium sulphates with silicates (Ruggeri). Similarly, the use by Stradivari of this inorganic fraction was showed in a study of Fulton and Schmidt, where calcium carbonate and potassium aluminosilicates were found in the wood of a cello [29]. Our results obtained from Ruggeri and Guarneri fragments were supported by Nagyvary and Ehrman [30] with a study performed on four wood finish samples of Stradivari, Ruggeri, Guarneri and a 18^{th} century Venetian viola, analysed by SEM-EDX. Thus, the practice of treating wood with inorganic salts seems to be common to a new Cremonese violin making school during the second part of the 17^{th} and all along the 18^{th} centuries. In fact, the technical differences highlighted between the master (Nicola Amati) and his pupils seem to indicate that

the new generation of violin makers developed a new method of wood treatment before to apply the varnish, according to a general approach that was adopted transversally in the coeval Cremonese production. The same holds for Guadagnini, who did not retained the techniques of his master Antonio Stradivari.

Regarding the wood, the modification of the tracheids highlighted in the fragments from the instruments by Amati and Guadagnini, seems to suggest a pre-treatment with the aim to remove the cellulose components in order to collapsing the tracheids and avoid the penetration of the subsequent materials in the wood structure [9, 22, 31]. The discussion about the earlier treatments of the wood before to finish the surfaces is still open: a first claim regarding some kind of special aqueous treatment for the wood was advanced by Nagyvary [22] in the form of SEM images of internal spruce sapwood samples. This research seems to validate our results. In contrast, Barlow and Woodhouse found nothing remarkable in their SEM study of the morphology of spruce samples from Italian musical instruments [9, 31]: the conclusion was not backed up by mineral analysis, which would have been the simplest way to prove the absence of aqueous treatment. Recently, Nagyvary et al. [32] carried out a study of maple wood from the backs of instruments made by Stradivari and Guarneri del Gesù in comparison with the maple from antique French and English instruments. The Italian samples revealed chemical modifications in the wood structures and the changes observed were supposed due to a procedure of boiling the wood in water. Thus, there could be no doubt that these particular woods were chemically treated: the only question concerns the specifics of the treatment.

Another relevant aspect that can be considered by investigating these fragments concerns the procedures of colouring the surfaces of the instruments. Here, the state of art is more complex and no homogeneity is found among the Cremonese apprentices of Amati. First of all, in the Guarneri and Guadagnini fragments, a thin coloured layer composed by inorganic iron-rich particles, applied under a colourless diterpenic varnish coating, was identified. Conversely, in the Ruggeri and in the two Stainer fragments, some iron-based inorganic particles (red ochre) dispersed in the outer varnish layers were found, as already reported for several coeval instruments [13, 33, 34].

Generally, inorganic pigments identified in Cremonese finishes include vermilion/cinnabar (mercury sulfide), orpiment (arsenic sulfide) and red earth (iron oxides) [35]. Arsenic was mentioned to being added to 18th century Italian varnishes, which has been detected even in the instruments by Stradivari [11, 36]. Moreover, as reported in Sacconi studies, Stradivari sometimes used cinnabar and Guarneri del Gesù added Venetian red (Fe_2O_3) to his varnishes [6]. However, the presence of iron pigments in two fragments confirm how those minerals can be considered a common pigment in old Italian violins, including Cremonese instruments by Ruggeri and Guarneri [30, 37], even if applied with two different procedures, as showed by our research. As reported in some scientific research, in one of the Stradivari violins, iron oxide was found alongside manganese oxide, indicating the possible use of umber earth [38]. This result appears strictly connected with the XRF analysis performed on the fragments, where Mn signal, associated with high counts of Fe, has been detected. Therefore, the presence of Mn and Fe in the fragments could indicate also the use of umber earth by those violin makers, even if is also known that iron and manganese were used as driers in fixed oil varnishes, too [39].

4. Conclusions

The combined of non-invasive and micro-destructive analytical investigations allowed us to identify the variety of materials and techniques used by the different violin-makers and has provided a precious and accurate state of art of the Cremonese historical manufacturing. The strategy employed by three coeval masters (Stainer, Ruggeri and Guarneri) to seal the wood porosity with a ground proteinaceous layer may indicate the sharing of common preparation procedures among Cremonese violin makers during the second half of 17th century. The evident differences between the apprentices and the master Amati could be representative of an evolution that involved materials, techniques and manufacturing models. On the other hand, similarities in wood treatment, without any trace of a proteinaceous ground layer, were instead observed in the fragments attributed to Nicola Amati and Lorenzo Guadagnini. This could be representative of a considerable geographical and artisanal variability, aspects that have marked the evolution of violin making production in different areas. The identification of iron-based earth pigments dispersed in the varnish layers (Stainer and Ruggeri) or spread with a binder (Guarneri and Guadagnini) confirmed how these techniques can be considered the most common procedures of colouring the surfaces of the Cremonese bowed string instruments. Therefore, the overall results obtained here by combining non-invasive and a micro-destructive analytical approaches, extended to both the organic and the inorganic components of the finishing layers, may represent a reference for investigations on further instruments of the Cremonese historical production.

References

[1] M. Clausi, G.M. Crisci, M.F. La Russa, M. Malagodi, A. Palermo, S.A. Ruffolo, J. Cult. Heritage (2011) doi: 10.1016/j.culher.2010.06.002

[2] M. Sedighi Gilani, J. Pflaum, S. Hartmann, R. Kaufmann, M. Baumgartner, F. Willis, M.R. Schwarze, Appl. Phys. A (2016) doi: 10.1007/s00339-016-9670-1

[3] F. Setragno, M. Zanoni, F. Antonacci, A. Sarti, M. Malagodi, T. Rovetta, C. Invernizzi, Acta Acust. united Ac (2017) doi: 10.3813/AAA.919035

[4] G. Fry, Italian Violin Varnish, reprint of the 1904 (Virtuoso Publ., Cape Coral, 1981)

[5] J. Michelman, Violin varnish (Joseph Michelman, Cincinnati, 1946)

[6] S.F. Sacconi, I Segreti di Stradivari (Libreria del Convegno, Cremona, 1972)

[7] W.M. Fulton, Turpentine Violin Varnish (San Diego, 1988)

[8] J.P. Echard, B. Lavédrine, J. Cult. Heritage (2008) doi: 10.1016/j.culher.2008.03.005

[9] C.Y. Barlow, J. Woodhouse, Catgut Acoust Soc J Series II 1, 4 (1989) pp. 2–9

[10] A. Von Bohlen, J Trace Microprobe Tech 17 (1999) pp. 177-187

[11] J.P. Echard, Spectrochim. Acta, Part B (2004) doi:10.1016/j.sab.2004.05.026

[12] G. Chiavari, S. Montalbani, V. Otero, Rapid Commun. Mass Spectrom (2008) doi: 10.1002/rcm.3785

[13] J.P. Echard, L. Bertrand, A. von Bohlen, A.-S.L Hô, C. Paris, L. Bellot-Gurlet, B. Soulier, A. Lattuati-Derieux, S. Thao, L. Robinet, B. Lavédrine, S. Vaiedelich, Angew. Chem. Int. Ed. (2010) doi: 10.1002/anie.200905131

[14] L. Rigon, E. Vallazza, F. Arfelli, R. Longo, D. Dreossi, A. Bergamaschi, B. Schmitt, R. Chen, M.A. Cova, R. Perabò, M. Fioravanti, L. Mancini, R.H. Menk, N. Sodini, G. Tromba, F. Zanini, e-Preservation Science 7 (2010) pp. 71-77

[15] M. Malagodi, C. Canevari, L. Bonizzoni, A. Galli, F. Maspero, M. Martini, Appl. Phys. A (2013) doi: 10.1007/s00339-013-7792-2

[16] F. Caruso, D. F. Chillura Martino, S. Saverwyns, M. Van Bos, L. Burgio, C. Di Stefano, G. Peschke, E. Caponetti, Microchem. J. (2014) doi: 10.1016/j.microc.2014.04.002

[17] L. Bonizzoni, C. Canevari, A. Galli, M. Gargano, N. Ludwig, M. Malagodi, T. Rovetta, Heritage Science (2014) doi: 10.1186/2050-7445-2-15

[18] C. Invernizzi, A. Daveri, T. Rovetta, M. Vagnini, M. Licchelli, F. Cacciatori, M. Malagodi, Microchem. J. (2016) doi: 10.1016/j.microc.2015.10.016

[19] G. Spotti, Gaetano e Pietro Sgarabotto. Liutai-Violin makers (1878-1990) (Turris, Cremona, 1991)

[20] K. Jalovec, Italian violin makers (Crown Publishers INC, New York, 1958)

[21] J. Nagyvary, Chem. Eng. News (1988) pp. 24-31

[22] J. Nagyvary, J.A. DiVerdi, N.L. Owen, H.D. Tolley, Nat (2006) doi: 10.1038/444565a.

[23] M.R. Derrick, D. Stulik, J.M. Landry, Infrared spectroscopy in conservation science. Scientific tools for conservation (The Getty Conservation Institute, Los Angeles, 1999)

[24] T. Rovetta, C. Canevari, L. Festa, M. Licchelli, S. Prati, M. Malagodi, Appl. Phys. A (2014) doi: 10.1007/s00339-014-8882-5

[25] M. Fellin, M. Negri, F. Mazzei, R. Zanuttini, Wood Res-Slovakia 59 (2014) pp. 533-546

[26] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, Pigment compendium. A dictionary and optical microscopy of historic pigments (Butterwoth Heinemann, Oxford, 2008)

[27] B. Brandmair, S.P. Greiner, J. Röhrmann, E. Blot, Stradivari varnish: scientific analysis of his finishing technique on selected instruments (Helmholz Publ. London, Munich, 2010)

[28] A. Bachmann, An Encyclopedia of the Violin (Da Capo Press, New York, 1966)

[29] W. Fulton and S. Schmidt, J. Violin Soc. Am. 9, 3 (1988) pp. 48-70

[30] J. Nagyvary and J.M. Ehrman, Naturwissenschaften 75 (1988) pp. 513–15

[31] C.Y. Barlow, J. Woodhouse, 13th RISO International Symposium on Materials Science: Modelling of Plastic Deformation and its Engineering Applications 9 (1992) pp. 213-219

[32] J. Nagyvary, Educ Chem 42, 4 (2005) pp. 96-98

[33] A. von Bohlen, F. Meyer, Spectrochim. Acta, Part B (1997) doi: 10.1016/S0584-8547(96)01596-0

[34] F. Caruso, S. Saverwyns · M. Van Bos, D. F. Chillura Martino, A.E. Ceulemans, J. de Valck, E. Caponetti, Appl Phys A (2012) doi 10.1007/s00339-011-6729-x

[35] B.H. Tai, J. Violin Soc. Am. 21, 1 (2007) pp. 119-44

[36] I.A. Cozio di Salabue, Count Ignazio Alessandro Cozio di Salabue: observations on the construction of stringed instruments and their adjustment 1804, 1805, 1809, 1810, 1816 (Taynton Press, Taynton, Oxford, 1987)

[37] J. Nagyvary, Das Musikinstrument 42, 6–7 (1993) pp. 107-11

[38] J.P. Échard, S. Vaiedelich, Quelques résultats d'analyses chimiques sur des vernis d'instruments d'Antonio Stradivari. De la peinture de chevalet à l'instrument de musique, vernis, liants et couleurs (Cité de la musique, Paris, 2008) pp. 104-13

[39] H.W. Chatfield, Varnish Constituents (Interscience, New York, 1944)

Captions

Fig. 1. Left: the six fragments considered in this study, attributed to: Nicola Amati (1), Jacobus Stainer (2, 3), Andrea Guarneri (4), Francesco Ruggeri known as “il Per” (5) and Lorenzo Guadagnini (6). Right: Gaetano Sgarabotto and a young pupil in the “varnish room” of the Violin-making School of Parma in the early 30’s

Fig. 2 UV-light optical microscopy (a) and SEM-BSE image (b) of the Amati fragment’s cross section. The varnish layer (V) applied on the treated maple wood (W) is clearly recognizable in the UV-light microphotography

Fig. 3 SEM image of the cross section of Stainer-A with two superimposed layers (P, V) applied on the untreated maple wood (a); EDX analysis performed on a micrometre inorganic iron-based particle dispersed in the external varnish layer (V) of the Stainer-A (b); cross section of Stainer-B fragment observed with optical microscopy under UV-light (c); µFTIR analysis performed on a micro-sample of the external varnish layer (V) of the Stainer-B fragment (d)

Fig. 4 UV-light optical microscopy of the Guarneri fragment’s cross section (a); SEM-EDX map of sulphur and calcium (gypsum) revealed in the finishing layers (b) and EDX analysis performed on a particle of gypsum identified in the ground coat (P) of the Guarneri fragment (c)

Fig. 5 UV-light optical microscopy (a) and a SEM-BSE image (c) of the Ruggeri fragment’s cross section; µFTIR analysis performed on the proteinaceous ground coat (b) and EDX analysis performed on a micrometre inorganic iron-based particle dispersed in the proteinaceous layer (P) of the Ruggeri fragment (d)

Fig. 6 UV-light optical microscopy (a) and a SEM-BSE image (b) of the Guadagnini fragment’s cross section; µFTIR analysis performed on the external varnish layer (V) of the Guadagnini fragment (c)