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A multi-technique chemical characterization of a Stradivari decorated violin top plate

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Abstract This paper focuses on the characterization of the materials of a violin top plate made by Antonio Stradivari (17th century), with different diagnostic techniques and with an integrated and non-destructive analytical methodology to study surface coatings and decorations. The UV-induced visible fluorescence, optical digital microscopy, ED-XRF associated with micro-FTIR spectroscopy analysis, and dendrochronology were performed. The investigations were aimed to identify the presence of original varnish layers and to characterize the composition of the decorations, either the inlaid purflings or the composite false-inlay strip between them. Several results were achieved: (i) evidence of the absence of varnish layers on the surface as a result of extended and inappropriate restoring; (ii) identification of the dye used for the black layers of the purflings; (iii) characterization of the black matrix and the white elements of the decoration. Furthermore, a dendrochronological dating was performed. A copy of the top plate was realized with materials similar to those identified on the Stradivari original; the same analyses performed on the original model were carried out on the same areas of the copy.

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1 Introduction

Antonio Stradivari, born in Cremona (Northern Italy) around 1644, is universally recognized as one of the most famous violin-makers in the world. During his long life, he and his apprentices realized more than a thousand violins, violas, cellos and other stringed instruments; in addition to those owned by the most important musical instrument museums of the world, many of them are preserved by collectors and still played by musicians [1]. The importance of his work lies in his craftsmanship, the quality of materials used and the finish of the surfaces. It is generally accepted that the sound of a violin is a results of the combination of the materials used (e.g., wood species, varnishes), the construction technique and the skill of the maker. The knowledge of the materials is also related to the aim to reproduce musical instruments with characteristics similar to the original ones. Throughout the last two centuries, several violin makers realized copies based on the Stradivari design in order to reproduce the tone quality [2]; as a consequence of this, many imitations and copies of the Stradivari instruments were made by excellent instrument makers. For all these reasons, in the last decades scientific studies were focused on the construction techniques and especially on the characteristics of the varnishes applied on the instrument surfaces

[3]. The term *varnish* is generally referred to as a "liquid which, when coated over a solid surface, dries to a transparent film" [4]; in the case of the violin, the varnish could be slightly colored, containing organic colorants, finely dispersed organic lakes or inorganic pigments. Research has been carried out in an attempt to identify the organic components; inorganic compounds, used by Stradivari in his varnishes either as components of a ground layer or mixed to the organic binders, were also analyzed [5, 6]. Since the earliest periods of musical instrument making, the decoration of the surface with different techniques has had an important influence on the aesthetic characteristics and consequently the prestige and the worth of an instrument. Usually Antonio Stradivari made elegantly simple instruments; nevertheless, during the different periods of his activity he realized some stringed and plucked instruments decorated with various cabinet making techniques: inlay, marquetry, wood etching and dying, similar to those used for furniture and precious wooden objects [7].

However, the greatest amount of scientific research has been conducted on the structure of the instruments and their finishing, very few on the decorations and the materials or the techniques used for making them [8]. Since the origins, the most typical decorations found on violins had the purpose of marking the outline of the top and back plates; the most usual consists of composite purflings made of three-layer strips of wood obtained by sticking together two black liners, generally made of ebony or black dyed wood, with a bright one placed between them [9, 10].

The decorated top plate, object of this work, was a component of a violin attributed to Antonio Stradivari on the basis of stylistic elements and dimensional characteristics [11]. It was probably part of a series of decorated instruments realized by the great violin maker between 1677 and 1722; the rest of the instrument no longer exists. The major characteristic of the top plate is the decoration of the border with a pattern composed by alternated white lozenges and circles on a dark background matrix.

The knowledge obtained from analyzing this top plate has helped researchers to have a better understanding of the kind of materials and techniques used by Stradivari and his contemporaries. Taking into consideration the historical value and importance of the top plate, the diagnostic research was totally carried out in very few hours using non-destructive techniques.

A great number of studies have been performed on different parts of the instrument in order to improve their statistic relevance on such heterogeneous materials while still preserving the integrity of the instrument.

Generally, for technical investigations on the materials used in historic artifacts a micro sampling procedure is required for a correct characterization of the materials, the identification of the stratigraphic layers or to study the particle distribution in the binders. When sampling is not possible, as in this case, the analytical and technical study of the artwork is necessarily limited to a non-invasive approach, with a mere surface characterization, without performing a deeper micro-chemical analysis on the samples or on the distribution of particles in the binder.

For this reason, all the results obtained allow us only to formulate hypotheses about the materials used by Stradivari and the nature of the organic binders. In order to confirm these hypotheses and to verify which "recipes" could have been used by Stradivari, a copy of the top plate was made, reproducing the presumed materials identified on the original instrument.

The traditional violin making technique was used to produce the decorative elements like the carvings along the surface of the top plate or the splicing of the three different colored layers of the purflings; the materials used, like the purfling strips or decoration elements, were prepared on the basis of traditional and ancient recipes according to the hypotheses formulated on the basis of analytical results.

At the end, non-invasive analyses were carried out on different areas of the decorations of the copy of the top plate, identical to the ones performed on the original one; then the results were compared.

2 Materials and methods

The analysis with UV-induced visible fluorescence was performed by means of preliminary direct observations and then photo shots were taken. The top plate was exposed to a Wood lamp with Philips TL-D 36 W BBL IPP low pressure Hg tubes (emission peak at 360 nm); the photo shooting of visible light fluorescence was carried out using a digital camera Nikon D90 with a Micro Nikkor 85 mm F3.5 objective, using a Kodak Wratten 2E filter (absorption at $\lambda < 415$ nm).

The optical microscopy analysis in visible light was performed with a portable digital microscope Dino Lite AM413T with 1280×1024 pixel resolution, at variable magnification ($10\times$, $50\times$, $200\times$) without lens changes.

The X-ray fluorescence analysis was performed using a portable Assing LITHOS 3000 spectrometer equipped with a Mo anode X-ray tube and Peltier-cooled Si-PIN detector. The radiation is monochromatic at Mo K_α energy by means of a Zr transmission filter (100 μm thickness). The irradiated spot on the sample is about 50 mm^2. The distance between the sample and the tube window, as well as between the sample and the detector, is 1.4 cm. The measuring conditions were maintained at 25 kV and 0.3 mA, with a 100 s analysis time.

The dimension of the top plate allowed us to perform FT-IR spectroscopy analysis through a Nicolet iN10 Thermo

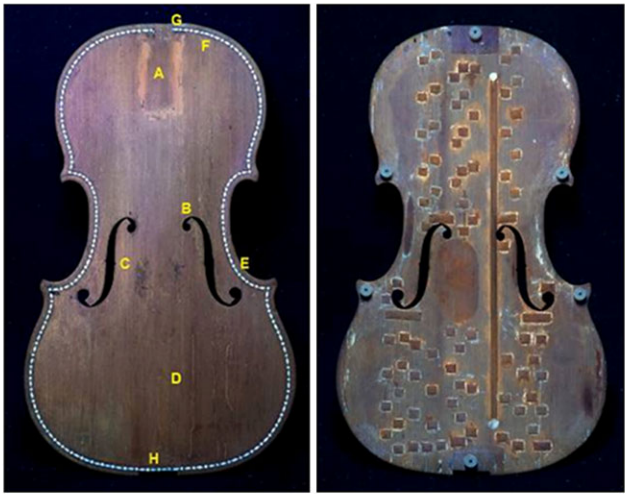

Fig. 1 Outside (*recto*), and inside (*verso*)—UV fluorescence (A-F-G fingerboard area; B-C-D top plate surfaces; E-H decoration areas)

Fischer micro FT-IR spectroscope, in ATR mode with germanium crystal; the spectral range was 4000–700 cm^{-1} and spectral resolution 4 cm^{-1}, measurements were carried out with a minimum of 32 scans.

A dendrochronological dating was performed on the wood, which was assigned to the Picea Abies species. The two halves of the lower part of the top plate were photographed (Treble and Bass sides) with a digital camera Nikon D90 with a Micro Nikkor 85 mm F3.5 objective in artificial light and the initial linear dimensions of the frames were 4288 × 2488 pixel. Dendrochronological plots of the growth density of the tree rings were obtained through the application of a software analysis procedure. The resulting curves were compared with a standard curve obtained from the average of the two curves ITAL24 (Larix Decidua trees of Fodara Vedla Alm from 1520 to 1990 A.D., noaa-tree-3558, Huesken W.; web ref. ftp://ftp.ncdc.noaa.gov/pub/data/paleo/treering/measurements/europe/ital024.rwl) and ITAL25 (Picea Abies trees of Fodara Vedla Alm from 1598 to 1990 A.D., noaa-tree-3559, Huesken W.; web ref. ftp://ftp.ncdc.noaa.gov/pub/data/paleo/treering/measurements/europe/ital025.rwl).

3 Results

3.1 Visual examination

Investigations by UV fluorescence and optical microscope techniques were carried out to evaluate the possible varnishes remaining and to study the coating morphologies of the decorated purflings.

Both sides of the top plate show a fluorescence background with dark patches, while the bright ones are probably due to proteinaceous materials, and it was possible to

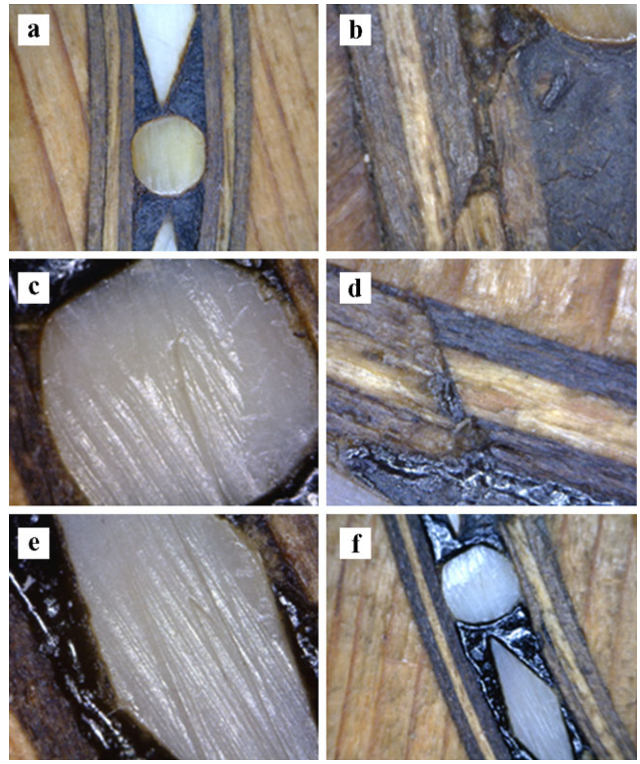

Fig. 2 Optical microscope examination of the decoration ((**a**) original decoration; (**b**) purfling detachments; (**c**) original white elements; (**d**) reconstructed decoration; (**e**–**f**) restored areas)

identify the presence of varnish layers only in the area corresponding to the fingerboard (Fig. 1a). Several traces of restorations, as varnish retouching and gap filling, result evident (Fig. 1b, c, d), as well as the restored segments of the decoration (Fig. 1e, f, g, h). The most meaningful areas on the basis of the UV results were further analyzed.

At the optical microscope, the decoration appeared composed by two external three-layered liners delimiting an internal strip with a false inlay (Fig. 2a). In general, the shrinkage of the decoration cause detachments and cracking and the thickness of the original purflings is dissimilar (Fig. 2b). The original white elements, like lozenges and circles, are included in a black matrix that appears to be made of coarse fragments of a dark material (Fig. 2c). The reconstructed segments of the decoration are easily recognizable as fragments of a few centimeters, with a more uniform thickness than the original ones and the dark layers are deep black (Fig. 2d). The restored areas of the false inlay show a deep black color with a glossy surface and an amorphous aspect with microscopic size bubbles and hollows (Fig. 2e): it is not leveled with unpolished contiguous surfaces, and it does not always fill the void around the white elements (Fig. 2f).

Table 1 Elements detected by XRF. The listed values correspond to the net intensity of the peak normalized to time and coherent scattering peak intensity

Point analysis	Description	K	Ca	Mn	Fe	Cu	Zn	Pb	Sr	Traces
1	Wood	0.05	0.23	0.05	0.21	0.10	0.12	#	#	
2	Wood	0.02	0.16	0.05	0.05	0.03	0.07	#	#	Ni
3	Inlaid purfling	0	0.55	#	1.21	0.24	0.04	0.15	0.29	K
4	Inlaid purfling	0.09	0.58	0.01	0.58	0.26	0.06	0.14	0.26	
5	Inlaid purfling	0.09	0.73	0.04	1.03	0.32	0.10	0.18	0.21	
6	Inlaid purfling	0.04	1.08	0.03	1.03	0.06	0.07	0.04	0.15	
7	Inlaid purfling	0.04	1.06	#	1.20	0.11	0.05	0.14	0.15	Ni
8	Inlaid purfling	0.09	0.92	0.02	1.41	0.16	0.08	0.17	0.22	
9	Inlaid purfling.	0.11	0.75	0.02	0.93	0.38	0.11	0.18	#	Sr
10	Inlaid purfling	0.05	0.82	0.05	0.86	0.31	0.06	0.19	0.19	

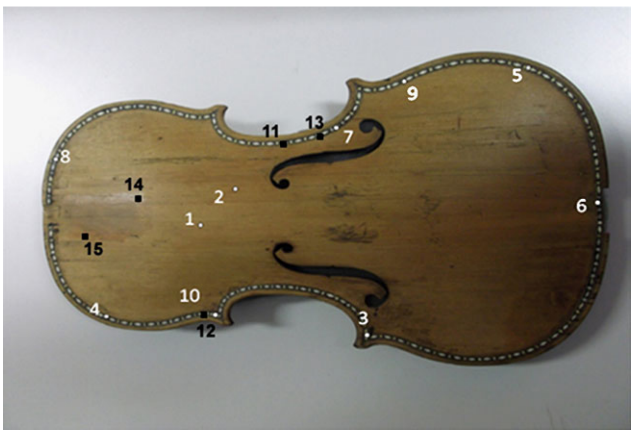

Fig. 3 General scheme of XRF (*white*) and FT-IR (*black*) point analyses

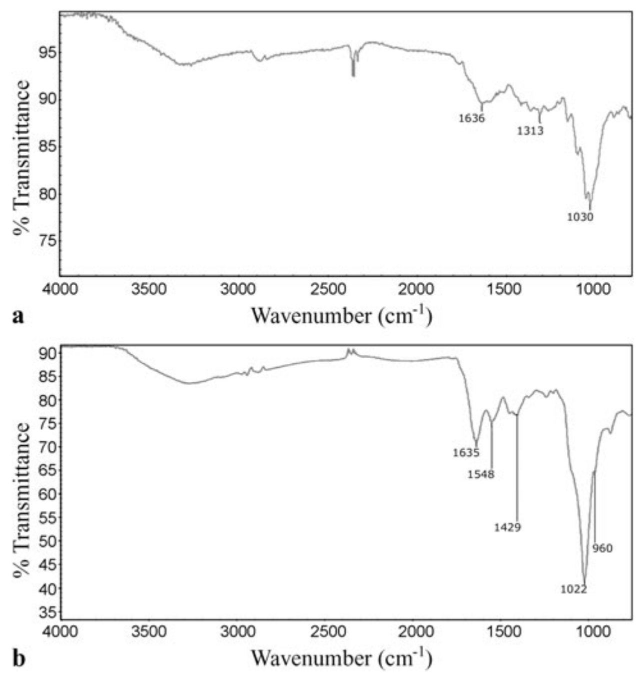

Fig. 4 FT-IR spectra: (**a**) wood surface; (**b**) white elements of decoration

3.2 Analyses of materials and dendrochronology dating

In order to characterize the decoration materials and varnish residuals, the Energy-Dispersive X-ray Fluorescence (ED-XRF) technique was applied together with the measurements performed with a micro FTIR spectroscopy. At first, XRF measurements (Fig. 3, 1 and 2 point analysis in Table 1) were performed on the top plate surface and the spectra showed a few trace elements referable to the natural wood. This result was supported by the FTIR absorptions, which can be assigned to the wood: the absorption peaks were 3300 cm^{-1} stretching of OH groups, 1736 cm^{-1} stretching of the C-O bond, present with a weak shoulder, 1596 cm^{-1} stretching of aromatic cycle of lignin with a weak absorption, 1423 cm^{-1} and 1040 cm^{-1} cellulose, 1155 cm^{-1} asymmetric stretching of bridging oxygen, and C-O-C glycosidic ether band at 1105 cm^{-1}, 898 cm^{-1} cellulose bond (Fig. 4a).

The XRF analyses have been performed on the different elements of the decoration (Fig. 3). It is worth mentioning that the diameter of the beam of the XRF instrument used is larger than the area of the inlaid purfling and the analyses also detected the elements of the lateral liners. As a consequence, we could not distinguish between the black matrix, the decorative white elements and the black lines of the purflings. Nonetheless, it is possible to affirm that the decoration area displays a higher concentration of calcium, with respect to the standard content detected in wood (Table 1) [12]. FTIR analyses were performed on the original white decorations (Fig. 3, point 12) and the restored areas (Fig. 3, point 13), highlighting a perfect overlap of the acquired spectra: the principal absorption peaks were at 1035 and 960 cm^{-1} associated to phosphate groups, and around

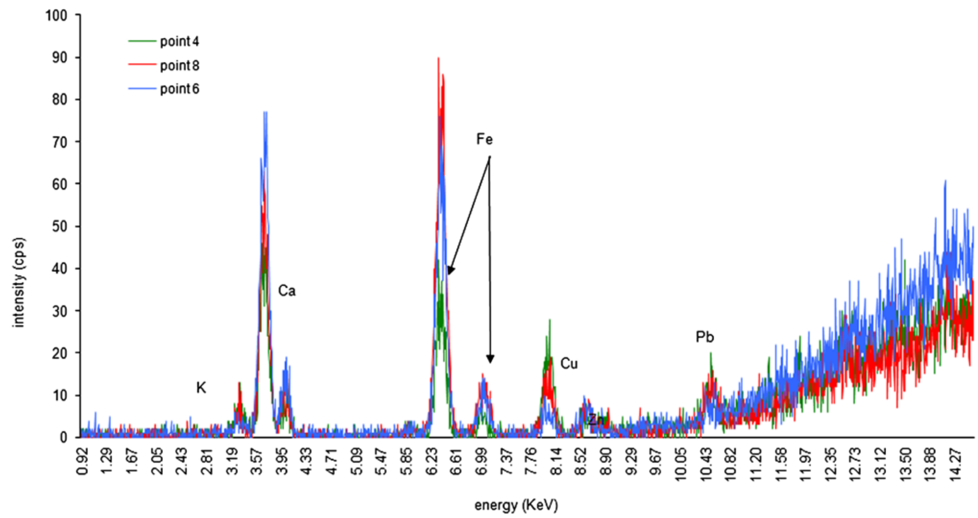

Fig. 5 XRF spectra of three different points on the decorated areas

Table 2 Ratio between the intensity of the peaks of characteristic elements. Starred measuring points refers to restored areas

Point of analysis	Cu/Fe	Pb/Fe	Cu/Zn	Zn/Fe
3	0.20	0.12	6.16	0.03
4	0.45	0.25	4.43	0.10
5	0.31	0.17	3.15	0.10
6*	0.06	0.04	0.92	0.06
7*	0.09	0.12	2.13	0.04
8*	0.12	0.12	2.06	0.06
9	0.41	0.20	3.34	0.12
10	0.36	0.22	4.94	0.07

1430 and 830 cm^{-1} together with the peak at 1635 cm^{-1}, ascribable to the presence of carbonates (Fig. 4b).

The XRF results related to the black wood of the purfling show amounts of Fe and Cu higher if compared with the natural wood content: these data could indicate the presence of a Fe-complex coloring material. Figure 5 shows the spectra detected on three different points of the inlay purfling, concerning both restored (measuring points 6, 7, and 8) and original areas (measuring points 3, 4, 5, 9, and 10). The relation between Cu, Fe, Pb and Zn is the most important parameter for the characterization of iron dye chemical composition [13]. For this reason, Cu/Fe, Pb/Fe, Cu/Zn and Zn/Fe ratios were taken into consideration as reported in Table 2. The diagram reported in Fig. 5 shows the compositional variation between the original (measuring point 4) and the restored (measuring points 6 and 8) areas of the inlaid purfling. The Cu/Zn and Cu/Fe ratios in the restored areas are significantly lower than in the original ones. Please note that Mn presence is not correlated to Fe, so that Mn does not result as an impurity of Fe compound.

The scatterplot (Fig. 6) also shows that, on the basis of the three elements ratio (Cu/Zn, Pb/Fe, Cu/Fe), the restored points 7 and 8 have a very similar composition, suggesting the use of the same material, while point 6 seems to be executed with a different composition. All the other measuring points, those claimed to be original, have very similar chemical compositions, apart from point 3, showing ratios in between the two main groups.

The analyses on the lateral black inlays, performed with the selective ATR spot, confirm the presence of a dye ascribable to an iron ink, characterized by the strong tannate peak around 1705 cm^{-1} and by the very strong iron-cellulose ring complex at about 1100 cm^{-1}, which alters the cellulose's ring profile (Fig. 7a), associated to an absorption at around 1470 cm $^{-1}$. Furthermore, the IR analyses performed on the black matrix of the decoration (Fig. 3, points 11 and 12) show a high affinity between the different spectra, with characteristic OH^- stretching absorption at 3200 cm^{-1} and glycoside bond at 1042 cm^{-1}, suggesting the presence of cellulosic material. The comparison of this spectrum with the ebony standard shows a perfect overlay, except for a weak absorption at 1635 cm^{-1}, ascribable to the stretching of the amidic carbonyl group (Fig. 7b).

In order to date the top plate, the wood was recognized as Picea Abies, and the provenance place can be assessed (taking into account the available sources and the market trends) around the Alps region. The date of the last ring is associated to the last visible ring of the analyzed sequence, considering

Table 3 Statistical data of the best synchronization results

Code	TBP	THO	GI	Overlap	Last ring date (a.D.)
Trebles	3.76	3.77	62.50	120	1659
Bass	1.53	2.27	50.50	94	1633
Whole plate	3.78	4.14	60.80	120	1659

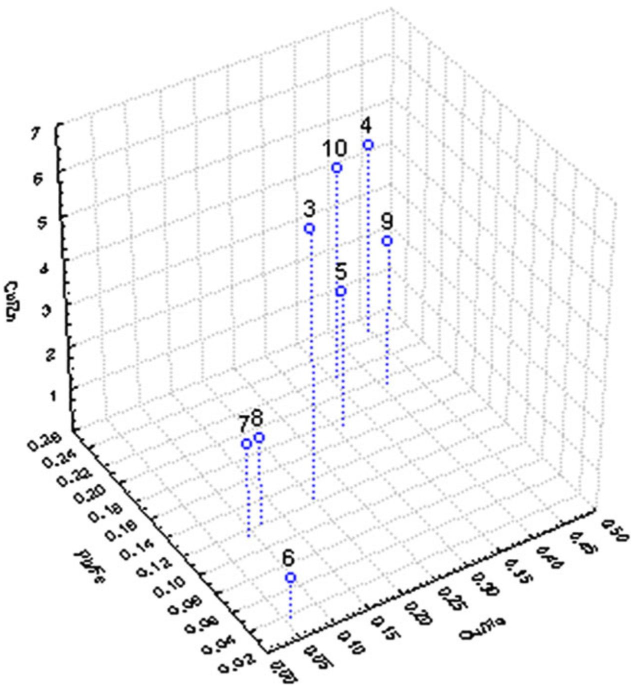

Fig. 6 3D scatter plot of Cu/Fe, Pb/Fe and Cu/Zn ratios

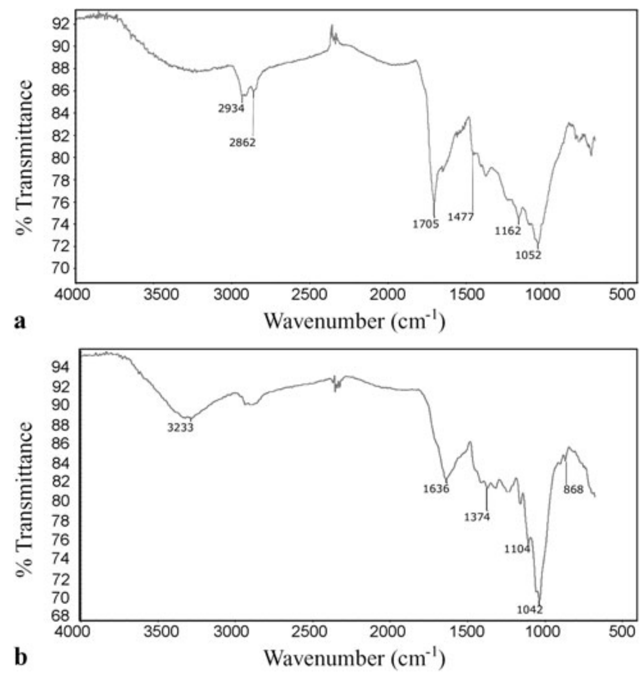

Fig. 7 IR spectra: (**a**) original black matrix; (**b**) original black purfling

as the first ring the one closer to the core. In Table 3 the best statistical parameters of the analyzed curves are shown, with the date referred to the last observable ring on the plate. The year 1659 a.D. represents the last date recorder by the tree rings on the plate, and so it is taken as a *terminus post quem* of the cut of the original tree.

3.3 The copy of the Stradivari top plate

The top plate was reproduced on the basis of Stradivari models, according with the violin making tradition techniques and using materials selected on the basis of the analyses performed on the original top plate. All the construction phases were carried out at Civica Scuola di Liuteria in Milan.

With the goal of dyeing the wooden strips of the purfling black, a traditional recipe was used: a thin strip of pear was put in a NaOH 0.1 M solution and boiled for one hour. After this treatment, the wood was rinsed carefully with water and put in a mixture with ground galls in a solution of water with ethanol (10 % in volume) and acetic acid (5 % in volume) in order to reproduce the most significant characteristics of wine and vinegar specified in the recipe. After 4 days the strips of wood were rinsed again and put in a solution containing a mixture of different sulfates ($FeSO_4$, $Fe_2(SO_4)_3$, $CuSO_4$, and $KAl(SO_4)_3$), with the aim of reproducing the chemical composition of the *roman vitriol* reported in literature; the solution was boiled for one hour and in the end the wood, which had turned black, was rinsed again with water and dried in the open air.

Once the black strips were ready, the purfling was assembled splicing together white and black wood layers with hide glue. Two grooves were carved all along the contour of the top plate and the purfling was inserted in them fixing it with hide glue. This procedure has been very difficult, mainly the step when the purfling was curved and inserted into the carving, because the dyed wood was stiff and fragile.

To realize the inner part of the decoration, at first the decorative elements were placed into a new groove carved in the spruce of the top plate between the purflings: all the white circles and lozenges were glued on the bottom of the new groove with hide glue, the same used for the purflings. The decorative elements were made of bone. The black matrix to complete the decoration was made mixing ebony powder with liquid hide glue to obtain a sort of black putty that was

Fig. 8 Copy of the Stradivari top plate

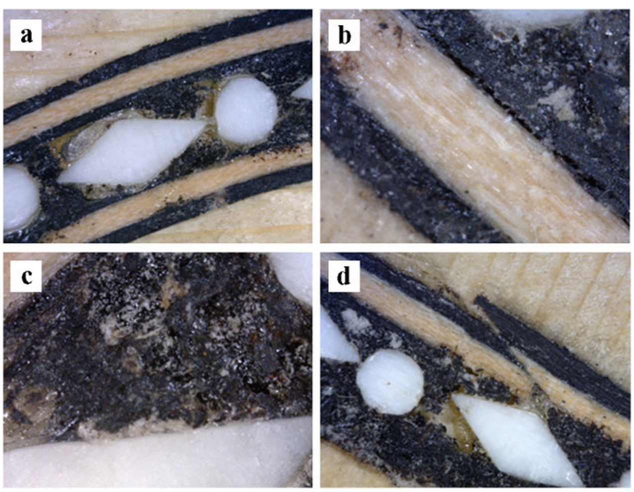

Fig. 9 Optical microscope examination of the copy top plate decoration ((**a**–**b**) decoration and purfling shrinkages; (**c**) black matrix de-cohesion; (**d**) yellow binder)

spread in the voids of the groove; the ebony powder was obtained scraping the wood with a file.

At the end, all the decoration strip was cleaned and smoothed to obtain a homogeneous surface (Fig. 8).

When the top plate copy was finished and ready, the diagnostic analyses performed on the original top plate were repeated on the copy in similar analytical conditions.

The visual examination of the purflings showed several detachments and cracking all along the decoration (Fig. 9a, b). The non-homogeneous width of the strips is evident in several areas and it seems to confirm the complexity of the realizing technique. A spontaneous shrinkage of the black matrix of the inner decoration strip was observed, with the consequent appearance of yellowish glue on the bottom, a phenomenon similar to that identified on the original decoration (Fig. 9d). This behavior could be due to the different volume contraction of the protein glue and the wood particles which is clearly visible even if only a very low amount of glue was used to prepare the black filler.

The ED-XRF analysis showed results comparable with those previously obtained from the original top plate. In Fig. 10a, the spectra obtained by the purflings of the original plate is compared with the spectra of the copy: most of all the Fe intensities are almost the same and the ratios with other metallic elements is not so different from those obtained on the original, which naturally depended on the dye recipe used. The principal differences are evident in the amount of elements like Cu, Zn and Pb, not detected on the copy but present in the Stradivari purfling. In this case, it is worth highlighting the intensities of calcium.

The IR spectra were similar and the analyses performed on the black matrix and on the white elements overlapped perfectly with those carried out on the original top plate. It is worth highlighting the result of the spectrum obtained from the analyses performed on the black strip of the purfling, where the tannate peak at 1704 cm^{-1}, a weak absorption at about 1100 cm^{-1} concerning the iron-cellulose ring complex and associated to an absorption at 1475 cm^{-1} are evident (Fig. 10b). The presence of the absorption at about 1635 cm^{-1} is ascribable to the stretching of the amidic group.

4 Discussion

At first, no varnish layers were observed using UV-induced fluorescence on the surfaces, except for a thin layer on the area which was under the fingerboard when a violin is mounted, highlighting that this Stradivari's top plate was hardly reworked, with the removal of all the traces of the original coatings. The evidence of different restoration and reworking operations was confirmed by means of optical microscopy that pointed out different retouched areas, reintegrations, minimal traces varnish and proteinic glues and gap fillings. Furthermore, presence of a dissimilar black binder in reintegrated segments of the decoration was detected: the material texture looks homogeneous, with a high glossy effect and good adherence to the white decorative elements. These first evaluations were confirmed by micro-FTIR and XRF analyses, which detected on the surface only characteristic wood spectra [14] without the presence of organic coating and the absence of elements with a high atomic number, especially lead, related to the presence of drying oil varnishes [15]. Some heavy element compounds were intentionally added to the siccative oils to enhance the

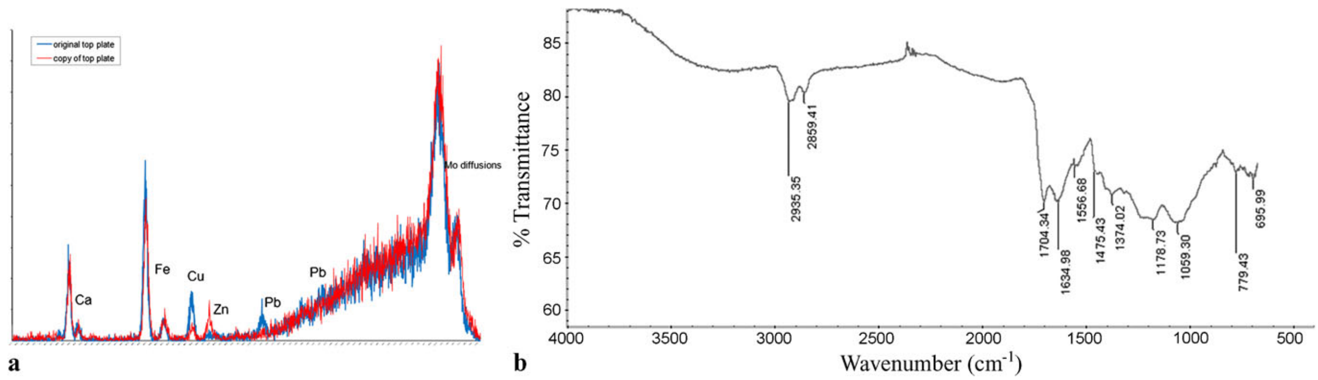

Fig. 10 XRF and FT-IR analyses performed on black wooden strip of the copy purfling

drying properties: these elements can accelerate the oxidative polymerization of siccative oils, with the consequent transition to the solid state, and enhance the properties of these materials as components of the varnishes and surface protectives for the artworks. The driers were generally metallic compounds or mineral pigments containing them; the most used in the past centuries were lead compounds [16]. It is now generally accepted that the ability of a metal compound to catalyze the oxidation of an oil and form a film depends on both the solubility and the dissociation of the metal ion in the oil; the pigments were mixed with different drying oils, such as linseed oil, to form an elastic film that encapsulates them [17]. To obtain a coating with the best properties, often siccative oils were mixed with terpenic resins. The observation of the top plate with the optical microscope was continued on the purflings, showing that the original black lines were diffusely cracked, with superficial detachments. The XRF analyses detected the presence of elements not directly ascribed to the wood, as in particular a fair amount of Fe, with traces of Cu. This result could be related to the presence of an iron dye as coloring agent used to obtain the black layers of the purflings [18].

In general, for this material, the relative amounts of Fe, Ni, Cu, Zn and Pb can be used as characterizers [19]. In fact, the ratio between Fe and Cu metals is different in the original and restored areas, indicating a different dye composition, or more probably the use of a different mordant. In the wood and in the original areas (see Table 1), the presence of manganese is ubiquitous and totally uncorrelated with the relative amounts of iron, copper and zinc in the black layers, suggesting a presence of this element in the wood matrix.

Depending on the origin, ferrous sulfate could be associated in the so called *vitriols* with various concentrations of other sulfates (Cu, Mn, Zn and Al). The spectra obtained with the FTIR technique confirmed the hypothesis of the presence of iron-gall dye used for the black inlay purflings, rather than an iron-logwood dye. In fact, in literature, the comparison between the spectra of iron logwood and of iron-gall showed different bands in the region of 1400/1500 cm^{-1} and the presence of a weak absorption at around 1477 cm^{-1} could be ascribable to the presence of an iron-gall ink or dye [20]. This kind of dye, on the basis of the ancient recipes, was generally prepared from tinctorial extracts (of galls or, later, of logwood, obtained boiling or soaking raw materials in water or other liquids), with the addition of vitriol, copperas (almost exclusively ferrous sulfate) or, later on in history, pure ferrous sulfate. Since the most ancient ingredients were not pure products and ratios among the components are not explicitly quoted in ancient recipes, the final result can vary a lot, the dye being an homemade product. Anyway, the relative sulfate composition of the different geographic types of *vitriol* is known [21]. As reported in literature [22], although ink was sometimes used to stain the surface, the wood could be colored with mordant dyes; so, the composition of the metallic mordant, and consequently of the dye, was different with respect to the geographic provenance.

A similar mordant dye was used for the black purflings layers of the restored areas; the analyses with the XRF data showed a different ratio between the principal elements.

With regard to the study of the black matrix, under optical microscope investigation it was possible to highlight a non-homogeneous structure with traces of organic materials, different fibrous grains and traces of a yellowish material, especially evident in the areas below or under the cracks. In different segment of the unrestored decoration, a cellulosic material and protein *medium* were detected by IR spectrometry and the perfect overlay between the reference ebony spectrum, with several peaks assigned to amidic groups, suggests as a ground ebony wood mixed probably with an animal glue could be used. Throughout history a great variety of natural products have been used in art and one of the most common applications of organic materials has been the use of proteinaceous materials, especially with the function of adhesives and gap fillers, in this last case with inert substances as addictives. The discovery of the employment by Stradivari of finely ground ebony mixed with an animal glue for the black matrix of the decoration is critical, first of all for preservation of the object; moreover, it can also help reveal working practices of the artist, even in order to rediscover the recipes and materials used in the past.

The results from IR and XRF spectroscopy techniques have also been employed for the characterization of the white decoration elements. As a matter of fact, the high amount of Ca highlighted by XRF, correlated to the IR spectra, confirmed that the material of the white lozenges and rounds of the decoration might be bone or, even more likely, ivory. This kind of material contains organic compounds: collagen, non-collagenous proteins, lipids and muco-polysaccharides and inorganic components, mostly calcium carbonate with apatite, similar to hydroxyapatite. White elements of this kind of decorative patterns were usually made of a bright wood (e.g. maple), mother of pearl, different kinds of ivory (e.g. from elephant, hippopotamus, walrus) or bone. Even if this was not a common practice, Stradivari and other makers in some cases used repetitive patterns made of small pieces of ivory in a dark matrix to decorate the top and back plates of their instruments; some of these can be considered sophisticated art pieces. An important reference instrument by Stradivari is the "Greffuhle" violin (1709, conserved at the Smithsonian Museum in Washington) with both plates decorated in a style very similar to that of the top plate objects of this article, composed of an elegant combination of circular and diamond shaped pieces of ivory.

All these results validate the versatility of Stradivari's workmanship, according with the traditions of ancient artists, craftsmen and musical instruments makers. Many historic string instruments for example guitars or mandolins, were richly decorated with various techniques of cabinet making: inlay, marquetry, wood etching and dyeing, similar to those used for furniture and precious wooden objects. Typical examples of this practice were the guitars by Matteo Sellas, a German instrument maker who worked in Venice at the beginning of XVIIth century and, later, the string instruments, lutes, viols, guitars, made by Joachim Tielke in Hamburg [23].

The high heterogeneity of the materials and the heavy reworking operations detected on the Stradivari top plate suggested that a dendrochronological analysis had to be performed, in order to confirm the possible manufacturing period of the violin. Dendrochronology assesses the most recent growth ring of the Stradivari top plate and dates it back to 1659 a.D., in agreement with the historical information. This dating technique showed to be potentially a good complement in a characterization protocol of wooden string instruments [24].

The analyses performed on the top plate copy seem to confirm the hypotheses corroborated during the analytical campaign on the original one. First of all it was important to correlate the optical microscope observations to on the copy and those on the original top plate. The visual examination shows morphological characteristics very similar to the original one, with a comparable texture of the materials, as detachments of the purflings or the shrinkage of the black matrix.

It is worth highlighting that the copy was made with not aged materials, while the Stradivari top plate is more than three hundred years old; consequently, the comparison has just to concern the principal behavior of the materials. However, XRF and IR results showed a strong correlation with those obtained from the original top plate: the almost perfect overlapping of the calcium emission registered in the XRF spectra confirm that the high Ca peak detected on the Stradivari instrument was related with the ivory of the white decorative elements. The high content of iron detected on both top plates seems to confirm that the iron-gall dye has been used to color the black layers of the purfling. The differences among the peaks and ratios of minor elements like Cu, Zn and Pb in the spectra obtained analyzing the original top plate and the copy which could be due to the use of the dye of the original purfling of true *vitriol*, which can include impurities and other compounds besides the most abundant iron sulfates, and not a mixture of pure reagents to simulate it.

5 Conclusions

The analytical investigation has provided several important insights about the manufacturing techniques of Antonio Stradivari and allowed for the formulation of a hypothesis about the recipes used by the important Luthier or by his suppliers to prepare the materials to decorate his instruments, representing an important step in the study of the materials used by violin makers during the second half of the 17th century in Northern Italy. The lack of varnish layers on the surface of the top plate, as a consequence of hard removal, was confirmed, and a lot of integrations were highlighted, like replacements of decorative elements of the false inlay and segments of the purflings. Ivory was detected as the principal material of the white elements of the decorations and the original black matrix was discovered to be constituted by powder of ground ebony with a proteinaceous binder, probably animal glue. The analyses carried out on the black matrix of the false inlay determined the iron-gall dye presence, confirming the use by Stradivari of the ancient techniques of wood coloring. The replaced white elements were made of ivory too. A high data interconnection approach with different analytical and non-destructive techniques was performed. The dendrochronological dating confirmed as the top plate realizing time complied to the Stradivari period.

A copy of the top plate was realized with material similar to those detected on the original and a new series of analyses was carried out, which led to interesting comparisons.

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