Authentication of ancient stringed musical instruments – the contribution of X-Ray Fluorescence analysis

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Abstract

The varnish from a supposed Stradivarius violin, recovered by Romanian Authorities in March 2009 was analyzed using X-Ray Fluorescence. Results were compared with the ones from literature, in order to try to authenticate the violin. Direct analysis was performed on the varnish instrument non-destructively, without any sampling - due its possible value. Analytical results obtained on violin varnish are discussed.

Key words: varnish, elemental analysis, XRF, violin

Introduction

For the past 300 years, the violins of the Cremonese luthiers (Stradivarius and Guarneri, especially) have excelled in molding a many-nuanced sound that seems to better express the intent of composers and musicians. Research into the production of high quality sound – and, indirectly, the authentication of most valuables instruments - has focused on a wide range of variables, such as the age and quality of used wood – including eventual chemical processing, the impact of varnish layers (see below), the arching design and contours and plate thickness. Extensive work have been done searching for the ideal wood properties: tests on various types of maples – from Norway to Bosnia – and on different soaking solution, e.g. Northern Italy mineral waters rich in calcium and magnesium salts.

Recently, a very interesting study was published on line (www.plosone.org) by Berend C. Stoel from the Department of Radiology, Division of Image Processing, Leiden University Medical Center The Netherlands and Terry M. Borman from Borman Violins, Fayetteville, Arkansas, United States. In this study they show that the vibration and sound radiation characteristics of a violin are determined by an instrument`s geometry and the material wood properties of the wood. New test methods allow the non-destructive examination of one of the key material properties, the wood density, at the growth ring level of detail. The densities of five classical and eight modern violins were compared using computed tomography and specially developed image processing software. No significant differences were found between the density of the modern and antiques violins, however the density difference between wood grains of early and late growth are significantly smaller in the classical Cremonese violins compared with modern violin, in both the top (Spruce) and back (Maple) plates (p=0.028 and 0.008, respectively). The mean density differential (SE) in the top plates of modern and classical violin was 274(26.6) and 183(11.7) gram/liter. For the back plates, the value were 128(2.6) and 115(2.0) gram /liter. These differences in density differentials may reflect similar changes in

stiffness distributions, which could directly impact vibrational efficacy or indirectly modify the sound radiation via altered damping characteristics. As a conclusion of their study – either of the mechanisms may help explain the acoustical differences between the classical and the modern violins.

The dendrochronology is also involved, especially to verify the theory of the use of 1400 – 1600 AD (the last micro-ice European period) Bosnian maple wood. The stringed instruments are coated with a protective layer that plays an aesthetical and – supposedly- acoustical role as well. These coatings are generally called "varnishes". The varnishes of old historical instruments are mixtures of natural organic substances (such as resin, oil, spirit, waxes, organic colorants) and, in lesser proportion, of inorganic substances added mainly to influence the color, the transparency, other physical properties and the drying time for the oil-based varnishes.

In the last years, the historical varnishes were studied and characterized by the content of chemical elements like P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Ag, Cd, Sn, Ba, and Pb using methods based on X-Ray Fluorescence (XRF). However, due to the small and variable thickness of the varnish layers, the analysis is performed also on chemical content of wood, so discrimination is necessary.

Experimental

The varnish of a supposed (label inside) Stradivarius violin recovered in March 2009, by Romanian Authorities during an anti-trafficking action and sent to our Archaeometry Laboratory was analyzed for possible authentication.

We focused on heavy elements (metals, especially) presented in the varnish, using a portable XRF spectrometer X-MET 3000 TX. For this instrument, the exciting X-ray beam is generated by a 40 kV tube with Rh–anode. The detection system is a PIN silicon diode detector with Peltier cooling. The resolution of the detector is 270 eV for the K_α line of Mn (5.89 keV). The measurement spot size is about 30 mm^2. The X-MET XRF analyzer has a Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage. Due the possible important value of the instrument, we performed only totally non-destructive analysis – no sampling at all.

Figure 1. The X-MET 3000 TX spectrometer while analyzing the violin.

Different color shades areas were analyzed, in order to see how the content of heavier elements varies versus color.

Several analyses were run in areas where varnish was worn or removed by repeated contact with the skin of musicians. These areas are the bottom part of the soundboard that the musician applies to his chin to hold the instrument when playing and the upper right part of the soundboard, over which the musician often places his left hand to play the highest notes.

Results and discussion

A set of 15 measurements was performed using the portable spectrometer. The results indicate two types of varnishes: one similar with those used in the 17th -18th centuries and another from early 20th century.

Three different types of varnishes were used for musical instruments from 17th century up to the middle of 19th century in Europe:

- Drying oil- based varnishes
- Essential oil-based varnishes
- Spirt varnishes

The most common siccative for these varnishes was litharge (PbO) with other lead compounds and more rarely white couperose, a zinc sulfate. The present of the lead (Pb) in the historical varnishes can be a reliable indicator for drying oil-based varnishes.

The lead was detected in the bottom-lateral-left area (figure 2), so, most probably, this is an original varnish from 17th – 18th century.

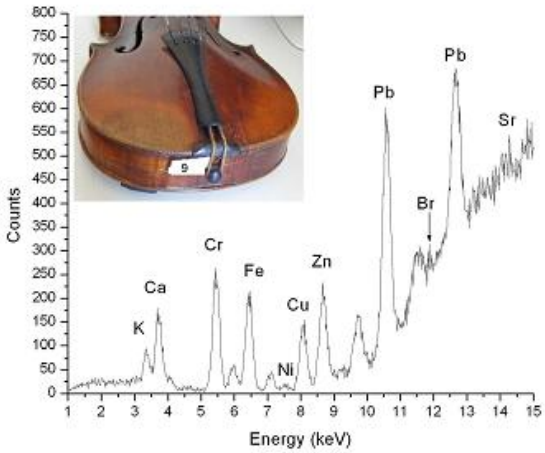

Figure 2. XRF spectrum of the historical varnish

The chromium – containing pigment – detected in the upper-lateral-right area (figure 3) could be originated from a retouching to obtain a similar hue to the original varnish (chromium-based pigments in varnish are specific for 20th century).

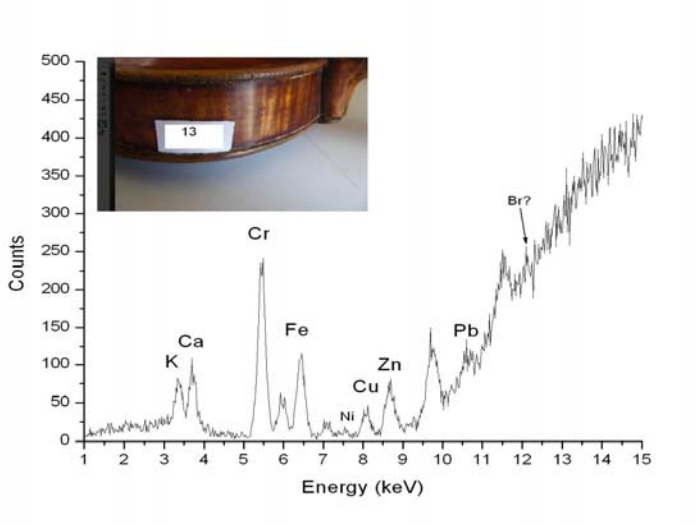

Figure 3. XRF spectrum of the modern varnish

Results have been compared with ones from published literature [1], [2]. Our conclusion is: old Pb-containing varnish – possible from 17th century, retouched with Cr-containing modern varnish in 20th century.

In the areas in which the skin of the musician was in direct contact with the instrument, we identified the characteristic elements of the sweat: potassium, calcium, zinc and copper. Here these elements are significant increased than in areas less or not exposed to sweat.

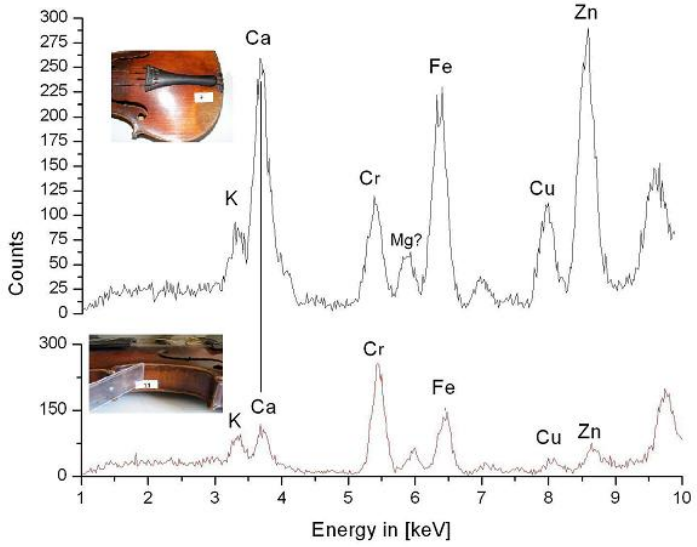

Figure 4. XRF spectra for a non-exposed (below) and exposed (above) to sweat areas

Conclusion

The varnish of this supposed Stradivarius violin was non-destructively investigated using a portable XRF spectrometer. The presence of siccative was deduced from the lead detected in some areas, and is an indicator of an old violin probably made in $17^{th} - 18^{th}$ centuries, retouched with an modern varnish - chromium containing pigments – in the first half of 20-th century..

References

[1] Alex von Bohlen, Historical Violin Varnishes Spectroscopic Studies and Characterization – Actes de la journee d`etude les vernis de violin – Cite de la Musique -2006, pg. 60

[2] J.P. Echard, B. Lavedrine, Review on the characterization of ancient stringed musical instrument varnishes and implementation on analytical strategy, Journal of Cultural Heritage 9(2008) 420-429