

Report

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Spatial resolved element analysis of historical violin varnishes using μ PIXE.

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Introduction

Violin varnishes, especially those of ancient Italian violin makers remain in a splendid quality over several centuries. The unknown recipes of these historical varnishes lead to a wide field of speculations. In the last decades several analytical approaches were contrived to elucidate the secret of Italian Masters [1-6 (only a selection)]. SEM-EDX, IR-Spectroscopy, Total Reflection X-ray spectrometry (TXRF) and other techniques have been applied. However, no reliable explanation could be deduced after elemental or molecular analyses of varnishes with respect to the original composition and to the pre-treatment of the wood.

The content of heavier 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 in historical varnishes has been studied in the recent past qualitatively and quantitatively using TXRF [7-9]. The element concentrations obtained by TXRF analysis correspond to the mean composition of small varnish flakes and do not contain any information about lateral or in-depth distribution of these elements. A line-scan, or even better an area map, performed on the transition wood/varnish on small splints will be of great importance for characterizing the elemental distribution in varnish layers and in a supposed interface between varnish and wood.

Experimental

Small samples, varnish flakes and small varnished wood pieces, were analyzed by means of μ PIXE (AGLAE facility at Louvre, Paris). Energy dispersive X-ray fluorescence spectra of different samples as well as line-scans and area maps were recorded. The multielement capability of the applied method and especially the possibility to record X-ray signals of light elements (F, Na, Mg, Al) under normal atmospheric condition (Fig.1) is demonstrated exemplarily in Fig. 2. For the analyses a proton beam diameter of about 20 μ m was chosen. All experiments were carried out with protons of 3 MeV energy while the analysis time was adjusted to a fixed total photon counting for the whole spectrum. Typically, measurements of about 4 minutes were done for each analysis point. Data was recorded and evaluated later by means of different software packages (GUPIX, AXIL, etc.).

In view of a possible quantification by means of an internal standard, some samples were doped with standard solutions. However, only preliminary measurements could be done during the measuring period.



Figure 1. Sample holder (left) supporting a small piece of varnished wood originally of a violin made by G.B. Ceruti around 1800 is presented to the proton beam (right).

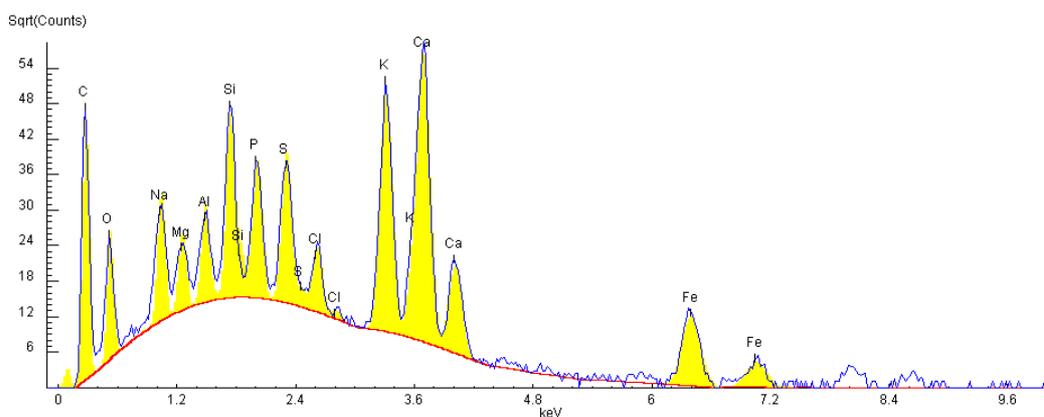


Figure 2. Typical μ PIXE spectrum obtained from a historical varnish.

Results and Discussion

Several modern and historical varnishes could be characterized by means of μ PIXE element analysis. A great palette of elements could be recorded simultaneously, as they are F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Sr, Ba, and Pb.

In contrast to the elements analyzed up to now in old varnishes by TXRF, the light elements F, Na, Mg, Al, and Si gave additional hints to the nature of the products used by different violin makers. Especially the special distribution assessed by line-scans and area maps gave an insight into the layered structure of some samples. Mono layers of varnish as well as composites could be detected. An example for a dual layer varnish system is presented in Fig. 3. It can be easily recognised that a ground varnish covers the wood and that a colour varnish covers the ground varnish. Both, the elemental composition and distribution as well as the thickness of the layers can be obtained from the μ PIXE analyses. Additionally, a possible lead interface layer may be present between ground varnish and wood material (cf. Fig. 3 lower spectra).

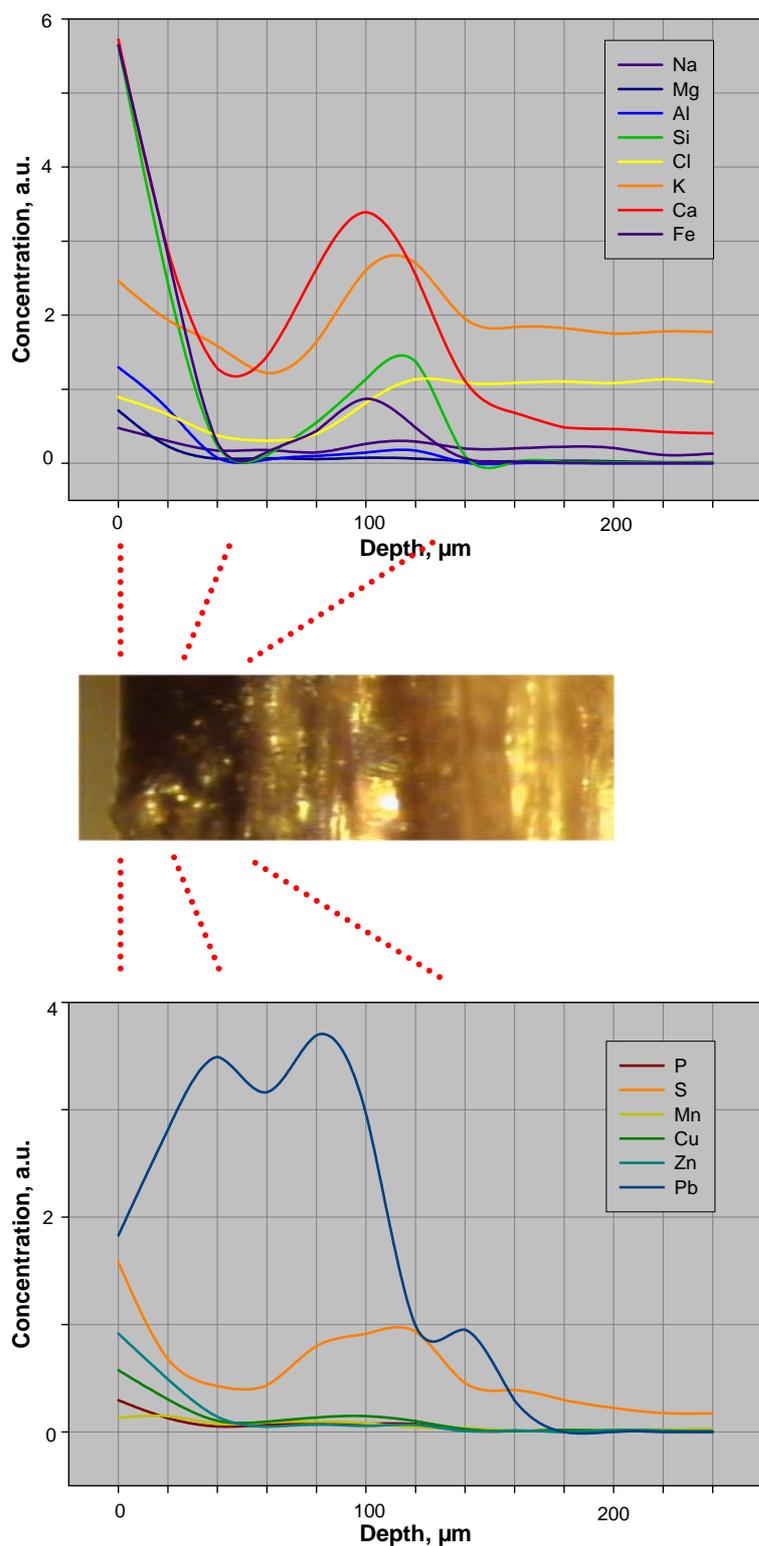


Figure 3. Results of μ PIXE analysis of a historical varnish. Element profiles obtained from a violin varnish applied by J.B. Ceruti to the table of a violin, about 1800. Two different layers can be recognized: the first, a color varnish, of about 50 μm thickness and a second, a ground varnish, of about 90 μm thickness cover the wood (represented from left to right). A mineral interface layer between the varnish and wood could not be confirmed, only a higher amount of lead could be observed.

An example for an area map obtained on a varnished piece of wood is shown in Fig. 4. For illustration of the capabilities and limitations of the analytical system only three elements are represented here. A higher spatial resolution would be advantageous for the representation of such thin layers as varnishes on historical musical instruments. However, a distinction of varnish and wood was possible by means of the obtained elemental distribution.

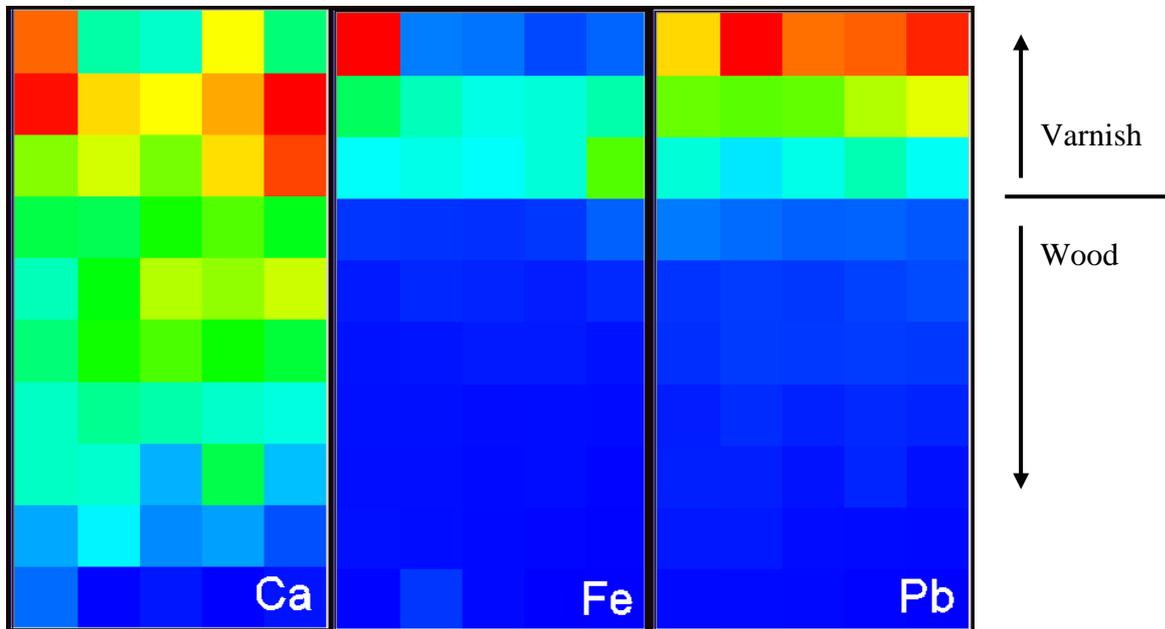


Figure 4. Area map representing distribution / concentration for Ca, Fe, and Pb over an area of 150 X 300 μm of a varnished piece of wood. Blue = low, Red = high.

With respect to a calibration procedure in view of accessing element concentration in the varnish layers, two regularly used methods of fundamental parameter calculations were applied: namely for infinitely thin and for infinitely thick samples. However, the measured samples do not belong to one of these groups. They are, due to the matrix wood and to the size of the samples, something in between of the extremes used for the calculations. A promising alternative method using an internal standardization could only be tested applying two elements (Co and Se). According to a first rough evaluation, a non optimal distribution of the standard elements added to the samples was obtained. Nevertheless, the method seems to be a promising alternative when dealing with samples like paper, parchment, wood and others. Prerequisite is a systematic study and the determination of the relative sensitivities for the elements in question. This will be presented in a proposal for the next measuring period.

Further, several samples were analyzed, e.g. from G.Guarneri, J.B. Guadagnini, M. Goffriller, Widhalm, etc. Over 200 single spectra and several area maps were recorded. The qualitative and quantitative evaluation of the analyses obtained during the measurement in Paris will be published soon.

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