

## ***Historical Violin Varnishes***

### ***Spectroscopic Studies and Characterization***

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*The recipes and preparation prescriptions for varnishes used by the prominent Italian violin makers of the past centuries remain unknown. Several studies have been conducted to elucidate the « secret of Stradivari's varnish ». These varnishes remain in every respect unequalled. Possibilities and limitations presented in modern studies of tiny flakes of historical varnishes applying microscopy and spectroscopy are discussed. Especially, analyses using total reflection X-ray fluorescence spectrometry (TXRF), proton induced X-ray emission (PIXE) and infrared spectroscopy (IR) are presented in detail.*

#### **I Introduction**

From the point of view of analytical chemistry historical varnishes are complex mixtures of natural products. The main components are organic substances such as drying oils, essential oils, resins, waxes, organic colorants, spirit, and others. Beside these major constituents some inorganic substances were added to control the properties of the varnish. All these products are of changing qualities, they are mostly of not controlled provenance and they contain a variety of impurities. The chemical analysis and the characterization of these kinds of products is a non-trivial work. Additionally, the nomenclature used for the components in old recipes is not unambiguous and the used units of weight are only of regional validity. A great variety of old formulas describing how to produce and how to prepare « by art » violin varnishes are known. Unfortunately, those of the most prominent Italian violin makers remain unknown. These varnishes remain unattained. Varnishes, especially those of musical instruments have been the subject of different kinds of investigation for long time. Many violin makers were looking in the past and are still looking today to reveal the secret or myth of Stradivari's varnish. Several historical varnishes have been studied and characterised by the content of heavier elements. Therefore, tiny flakes were directly analysed by total reflection X-ray fluorescence spectrometry TXRF [1-5], by X-ray fluorescence (XRF) [6], by scanning electron microprobe with X-ray emission spectroscopy (SEM-EDX) [7, 8], by proton induced X-ray emission (PIXE) and by infrared spectroscopy (IR) [9, 10]. A description of these methods can be consulted elsewhere [11]. For demonstrating the capability of these techniques some TXRF, IR and PIXE examples will be presented and discussed in the following pages.

## II Samples and Sampling

Small flakes of varnishes were collected from instruments under restoration by the aid of a clean scalpel. It is of primordial importance to sample a place clean and free of cracks. To avoid a possible contamination of the tiny samples with dust or dirt, they have to be put into a small piece of aluminium foil or white paper for the transport to the laboratory. Plastic containers are not suitable when IR analyses are planned. The softeners added to several plastics are able to penetrate the varnish flakes and disturb the IR spectra. Once in the laboratory the analysis by TXRF does not require any sample treatment, the samples only have to be placed in the centre of the quartz glass or plastic support [4]. Mostly they are analyzed between 100 s and 200 s by TXRF.

## III Examples

In Figure 1 a typical TXRF spectrum of an historical varnish is represented. The ordinate (y-scale) represents the number of counts acquired during the time of analysis, mostly between 100 s and 200 s. The abscissa (x-scale) represents the energy of the collected X-rays originating from the sample. These energies are unambiguous and each element has a typical pattern, a characteristic position in the spectrum. For that reason we can recognise all elements present in a sample. In this specific case a spectrum of a varnish applied to a cello by Antonio Stradivari is shown.

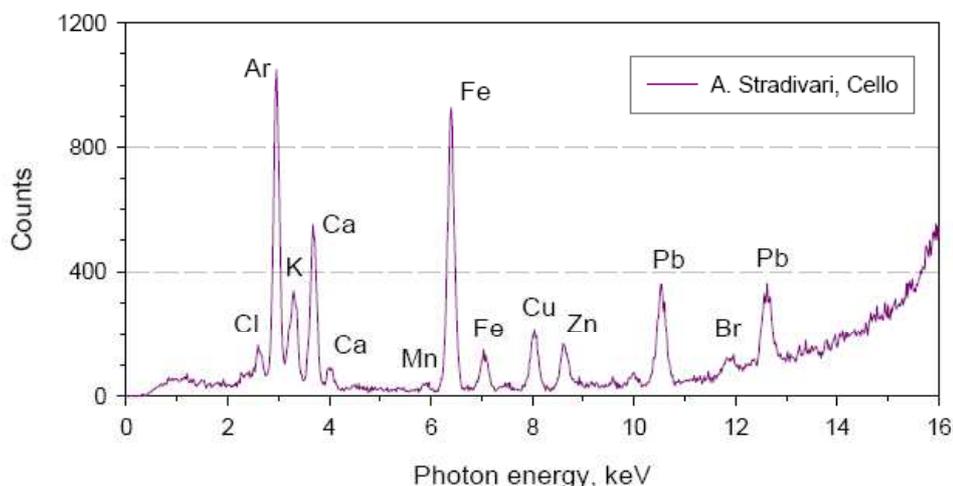


Figure 1. Element pattern detected by TXRF of a varnish applied by Antonio Stradivari to a cello.

In general elements with atomic numbers higher than 14 (silicon) can be detected simultaneously by TXRF. That means that we do not have any information of the most frequent elements in the varnishes. These elements (H, C, O, N, etc.) are the main constituents of the organic materials contained in the

varnish. They can be detected embedded in the molecular structure by molecular spectroscopy, e.g. IR spectroscopy [10].

The detected elements reflect the elemental distribution in products of natural provenance with only one exception: the lead. This element is present in a much higher concentration as its abundance in nature. This fact suggests an intentional addition of this element (Pb) to the varnish by the varnish maker to produce a certain chemical reaction. Unfortunately, today we know that lead is only a hint but not a proof for the use of an oil-based varnish [5].

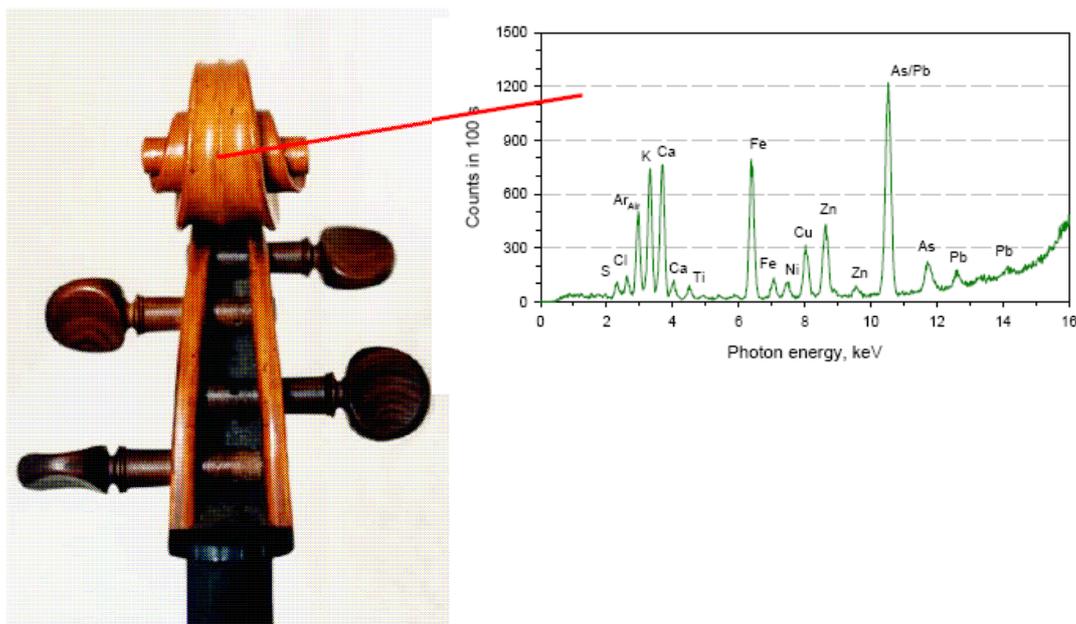


Figure 2. Scroll of a cello made by L. Mangin, 19<sup>th</sup> century and TXRF spectrum of the original varnish.

Figure 2 shows the scroll of a cello made by Louis Mangin, Paris, in the 19<sup>th</sup> century. The instrument shows several scratches on the varnish as is normal for an instrument regularly used for concerts. The violin maker had some doubts about the originality of the neck and the scroll of the instrument, so that two small samples of less than 20  $\mu\text{g}$  mass each were taken by the aid of a clean scalpel. Afterwards, the flakes were analyzed by TXRF. The first sample was taken of the scroll and the second of the side of the cello, which was supposed to be in original condition since the instrument was finished by Mangin. A spectrum of the varnish of the scroll as well as the results of TXRF analysis is shown in Figure 2 and Table 1, respectively.

	<b>Scroll</b> % rel.	<b>Side</b> % rel.
<b>S</b>	13.4	8.4
<b>Cl</b>	16.0	20.7
<b>K</b>	30.1	29.7
<b>Ca</b>	24.3	22.0
<b>Ti</b>	1.3	0.8
<b>Mn</b>	0.2	0.5
<b>Fe</b>	6.2	11.0
<b>Ni</b>	0.5	0.1
<b>Cu</b>	1.4	0.5
<b>Zn</b>	1.8	2.0
<b>As</b>	3.7	3.8
<b>Ag</b>	0.5	-
<b>Pb</b>	0.7	0.5

Table 1: Mangin cello

The varnish flake taken from the scroll and the piece taken from the side are of similar elemental composition. The varnish from the side of the cello contains significantly higher amounts of Mn, Fe, and Pb. These elements are commonly connected to some additives: e.g. earth pigments such as Ochre, Terra di Sienna, Kassler Brown, etc. or are connected to Pb containing pigments or siccatives such as Massicot, White Lead or Red Lead. However, the elements Ni, Cu, and Ag are significantly higher in the varnish of the scroll. This finding can be attributed to metal abrasion of the strings in the close vicinity of the scroll leading to contamination of the varnish. However, all these discussed elements are present in small amounts. The main elements such as Cl, K, Ca, Ti, Zn, and As are present in similar high amounts (their sum is 77.2 % and 79.0 % respectively) and lead to the conclusion that both varnishes are from the same original batch. In contrast to the cello made by Mangin, the original varnish of the back and of a retouching of the neck of a violin made by Ch. & S. Thompson, London ca. 1780, show clear differences. The superimposed TXRF spectra (Figure 3) of both varnishes illustrate the results of the micro analyses using only some  $\mu\text{g}$  samples. Clear differences for nearly all elements can be observed except for S, Cl, and Ni. Some modern chromium containing pigments seem to be added to the varnish of the retouching to obtain a similar hue of the original varnish.

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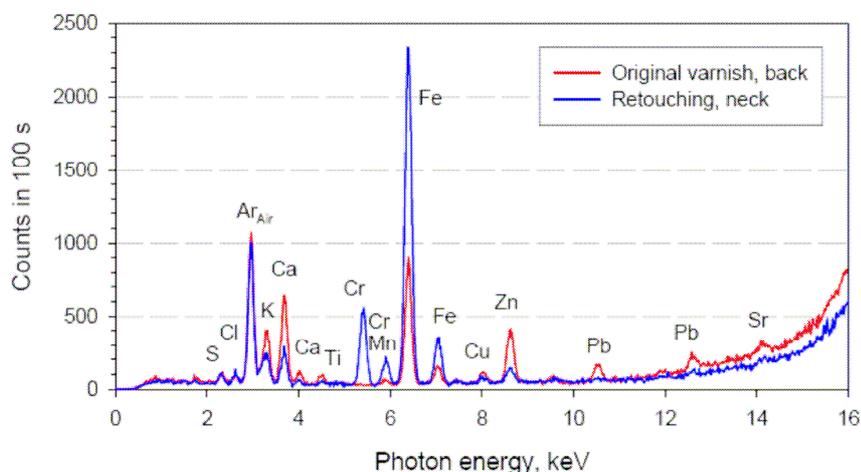


Figure 3. TXRF spectra of a violin varnish and a retouching on a violin made by Th. & S. Thompson, London, about 1780.

The following example was for long time a miracle. We were not able to find the right explanation concerning the presence of two elements found in a serie of different varnishes of prominent violin makers like Andrea Guarneri and Leopold Widhalm. The TXRF spectrum shown in Figure 4 was recorded from a tiny flake taken from the scroll of a cello made by Guarneri. The energy range is enlarged until 32 keV for covering the area on which X-ray lines from elements niobium and barium appear. The tin lines are obvious and the intensity (number of counts) is high when compared with the other detected elements. No consistent explanation could be found for the presence of tin and of silicon, which appears as a very weak signal because of its low sensitivity in TXRF. Should it be the secret of the wonderful cherry red varnish? And what is the function of tin in the Widhalm brown varnish? A useful hint came years later when analysing ceramic objects from which moulds were taken by the aid of a modern silicon-based rubber suitable for exact rebuilding surfaces. These objects show the strong tin signals in contrast to those which had not been copied. We decided to take a mould of a 100-years old back of a violin and compare the varnish before and after the copy. The results of TXRF and IR analyses were clear: Silicon and tin are contained in the hardener of the rubber. Additionally, the similarities between the IR analyses of the suspicious varnishes from Guarneri and Widhalm (Figure 5.) and those of our experiment were surprising [10]. The impact of the use of modern polymers for copying varnished surfaces cannot be judged today. We have no knowledge about the interaction of the modern organic compounds and the varnishes after several years. However, we are able to detect, by making analysis of the varnishes, if the moulds of instruments were taken or not.

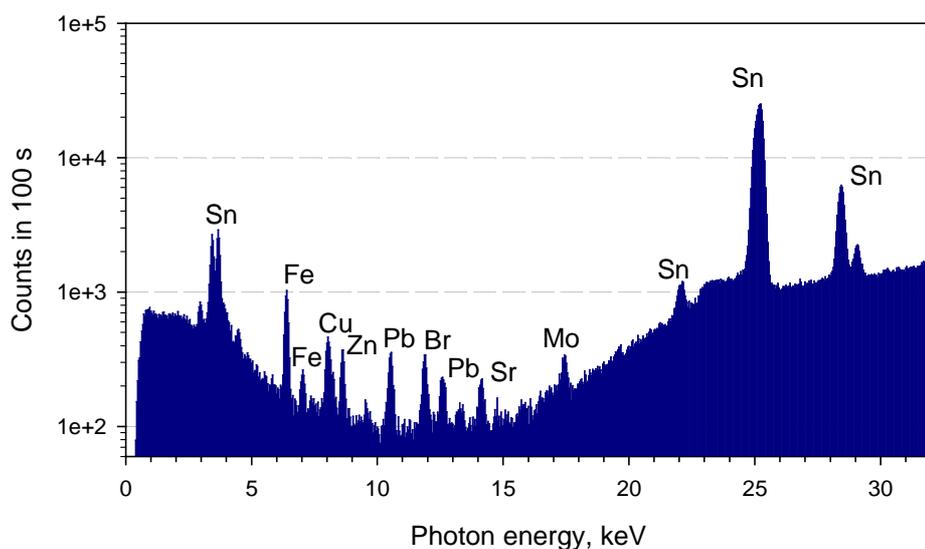


Figure 4. TXRF spectrum of a A. Guarneri varnish, cello about 1700, scroll. The tin signals are from a silicon rubber used for taking a mould of the scroll.

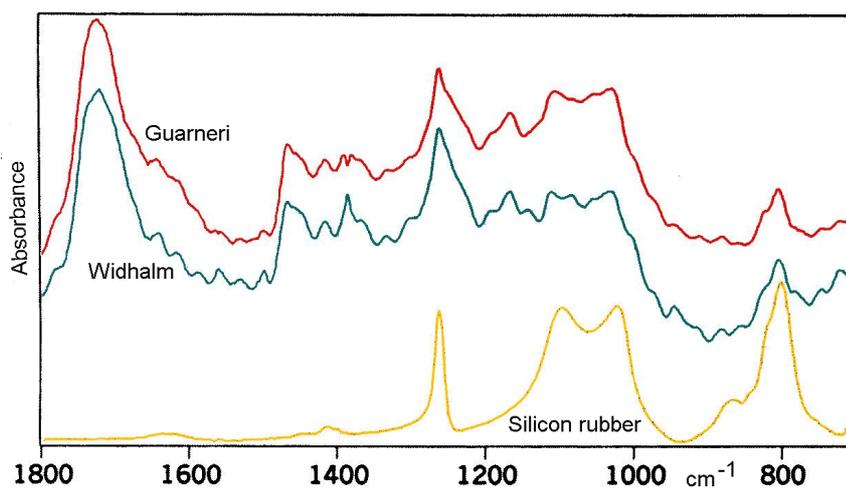


Figure 5. Similar IR spectra were obtained from a Widhalm and a Guarneri violin. Both surfaces have been copied with the aid of a silicon rubber (after [10]).

Infrared spectra contain information about the molecular structure of organic and sometimes also of inorganic compounds of varnishes. It is possible to compare the signals – absorption bands – of the varnish and of the organic components like fatty oils, waxes, resins, etc. The characterization of varnishes by using IR spectroscopy allows a coarse estimation of the ingredients used for preparation. The ageing of the varnish is obstructing the interpretation of the signals. The example shown in Figure 6 represents the superposition of a modern varnish produced by Christoph Götting (United Kingdom 2005) and the historical varnish of a cello made by Mateo Goffriller around 1700. The pattern is similar except the broad peak between 1000 and 1300  $\text{cm}^{-1}$  due to some wood fibers adhered to the Goffriller varnish.

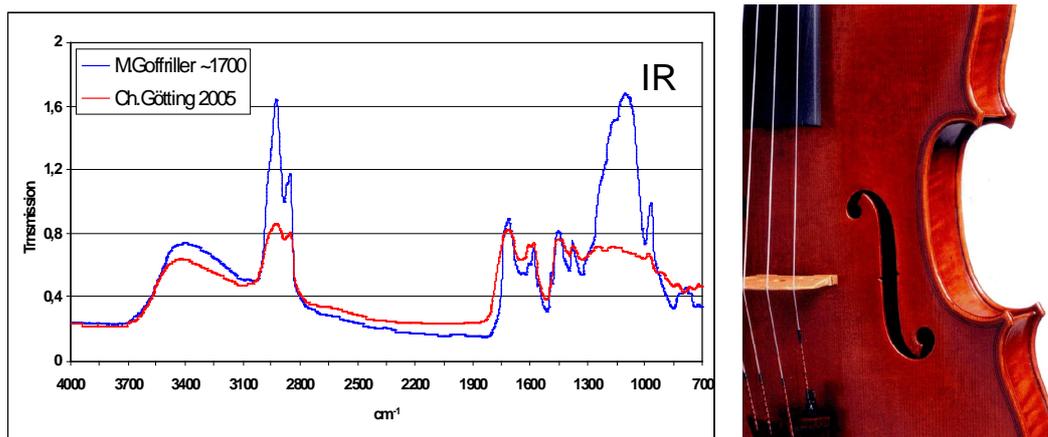


Figure 6. IR-spectra of a modern (C. Götting) and of an historical varnish (M. Goffriller). Similarities are obvious. Right: Detail of a modern viola (C. Götting).

Emile Français, a prominent French violin maker had some trouble with his oil-based varnishes. Some of the instruments made around the years 1948 show today, more than 50 years later, a sticky surface. First analyses of the varnishes of violin (inventory number E.984.7.2) and viola (inventory number E.984.7.3) stored in the Cité de la musique in Paris were compared with the analysis of a varnish used by Français two years later. The product of 1950 was used to varnish a cello. This younger varnish is dry and shows a fine dark red hue. The element ratios of the three varnishes are presented in Figure 7. The main differences can be observed in the presence of manganese and cobalt in the cello from 1950. Additionally, the amount of lead in the varnish is significantly lower. An interesting observation is that the ratios of the elements in the younger varnish are very close to those stated by the German DIN-Norm to be best for siccatives used for drying-oil based varnishes. The question remains open, if Emile Français used a commercially available varnish or if the instrument was varnished later using such a product.

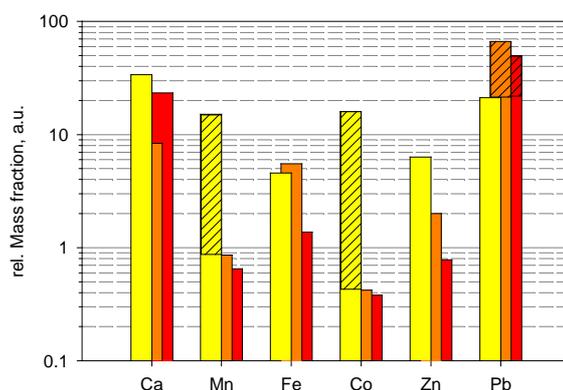


Figure 7. The element pattern of the older varnishes is marked in red and orange, the younger in yellow. The main differences between the two older and the younger varnish can be clearly observed in the relative element abundance detected by TXRF analysis.

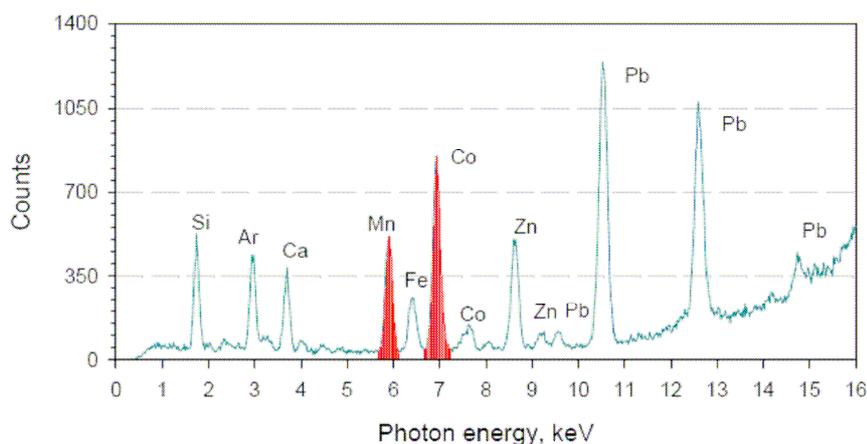


Figure 8. TXRF spectrum of the varnish used 1950 by E. Français. The strong signals of Mn and Co indicate the use of a modern siccatif for drying oils.

#### IV Outlook

The contribution achieved by modern methods of instrumental analytical chemistry for studies related to historical varnish is useful and opens new perspectives. Mostly, it is not possible to deduce all components of the varnishes from the results obtained from the analyses. Uncertainties in the interpretation of IR spectra due to an unknown and not documented ageing of the individual varnish are common. That means that we are not able to reconstruct the complete list of ingredients of the historical recipes. Further, we are not able to deduce any suggestion about the preparation of varnishes 'by art'. This procedure remains unknown. Nevertheless, modern alterations like retouching and taking moulds from the varnished surfaces can be detected without any special effort.

The systematic screening of historical varnishes might present in the future a more detailed characterization of regional differences as well as chronological dependences. Therefore a large number of varnishes should be analyzed in order to reach a higher level of confidence.

#### Literature

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