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The use of XRF imaging for the chemical discrimination of iron-gall ink inscriptions: a case study in Stradivari's workshop

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Abstract

X-ray fluorescence (XRF) analysis is a powerful approach to discriminate iron-gall inks from different inscriptions. The representativeness of spot measurements is though often impaired by the material history and conservation state of historical artefacts bearing such inscriptions. The method proposed here, using a XRF scanner, not only improved the readability of inscriptions, thanks to the enhanced contrast offered by chemical maps, but also allowed the evaluation of iron, copper and zinc contents of the inks, by the optimized selection in MA-XRF maps of more than 1000 spectra from each inked area, representing an equivalent analytical surface of several square-millimetres. In addition, the quantitative calibration of the system based on the thin target approximation allowed calculating these elements concentration. This method, applied to a series of ink inscriptions on a set of artefacts from Stradivari's workshop (active from 1666 to 1743) now in the collection of the Musée de la musique (Paris, France), offers a complementary route to the more conventional palaeography- and graphology-based approaches for the potential identification of the authors of the inscriptions.

Keywords: elemental analysis, imaging, iron-gall inks, Stradivarius, XRF

1. INTRODUCTION

In western countries, iron gall inks have been most widely used for writing. They are prepared by mixing iron sulphates salts, often referred to as “vitriol”, with aqueous extracts of gallnuts (growths produced by some trees, especially oaks, after the bites of certain insects) [1]. These extracts are rich in carboxyphenolic acids, such as gallic acid. In the presence of oxygen, iron (II) oxidizes to iron (III) that reacts with gallic acid, forming a black iron (III) gallate precipitate [2]. Gum arabic is usually added as a binder to make the ink more suitable for writing with a quill. The iron sulphate salts used in the preparation of inks may contain varying proportions of other metal residues, such as copper, zinc, manganese, lead. Indeed, the mineralogy of iron sulphates includes a great variety of different phases including mixed-phases [3]. Moreover, melantherite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) can form solid solutions with goslarite ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and boothite ($\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$), meaning that green vitriol, supposed to be melantherite, may also contain significant proportions of zinc and copper [3,4].

Therefore the addition of other metals than iron may not necessarily be the intention of ink makers. It yet constitutes markers that helps distinguishing between different inks.

Iron gall inks may be characterized by different techniques, such as FTIR or Raman spectroscopy [5]. Their elemental composition has been the subject of several studies, dealing mostly with Proton Induced X-ray Analysis [6-8], and X-ray fluorescence (XRF) [9,10] two techniques leading to both qualitative and quantitative data. These analyses are often performed locally using a probe and a spot measurement approach, the signal being averaged to the size of the probe. However the ink distribution can be relatively uneven as it follows the support heterogeneities, the pressure of the hand during application, the paper size, etc. To achieve reliable quantitative measurements, a common practice is to take several records and average them, which is time consuming and raises the question of how many points to consider for being representative of the whole.



FIGURE 1. Visible pictures of (a) the six inner wooden forms, (b) a detail of an inscription on the form E.901.1, and (c) four of the eight smaller items with inscriptions. Collection Musée de la musique, Paris, France. Photos (a) C. Giordan, (b, c) Claude Germain © Cité de la musique - Philharmonie de Paris.

The last few years have seen the development of XRF scanners. Beyond the obvious potential of this imaging technique [11,12], it is possible to consider the collection of thousands of spectra and thus increase the representativeness of the results. More generally, the development of imaging techniques revealing heterogeneity of artefacts and materials is bringing up new approaches to discuss the methods of assessing composition of heterogeneous and complex materials, in particular in the field of heritage materials [13].

The present work investigates the potential of XRF mapping in terms of spatial selection of the signals of the whole inked area of an inscription, thus enabling the study of the composition of the ink not only qualitatively but also quantitatively. This approach was applied to attempt distinguishing different groups in a particularly complex corpus of ink inscriptions on wooden objects from Stradivari's workshop.

2. CORPUS AND HISTORY

The collection of the *Musée de la musique* (*Cité de la musique – Philharmonie de Paris, France*) includes a set of wooden artefacts (Figure 1), which were used as tools in the workshop of the instrument maker Antonio Stradivari (*ca.*1644-1737). Many of them bear short inscriptions in ink, directly applied onto the wood.

Their provenance (*i.e.* the history of ownership) does not allow identifying a single possible author for each inscription, but only a short list of five persons spanning over two centuries.

Stradivari's workshop was active in Cremona (Italy) from 1666 until the death of Antonio's sons Omobono in 1742 and Francesco in 1743. The only surviving son of the celebrated *liutaio* was named Paolo, a merchant with no skill in instrument making. Three decades later, in 1774-75, Paolo Stradivari sold the whole remaining set of tools, templates and documents from the instrument-making workshop founded by his father, as well as a number of violins of the workshop, to Ignassio Alessandro Cozio, Earl of Salabue (1755-1840). Cozio may be considered as the first scholar who specialized in the history of violin-making, dedicating his fortune to the purchasing of 16th to 18th c. violins — with a strong inclination for Stradivari's instruments — and about forty years of his life to the understanding of the design, measurements, construction techniques, etc. developed by Stradivari throughout his career [14,15]. His handwritten notes and book projects (left unpublished during his lifetime) are now kept in the *Biblioteca Statale di Cremona*. At his death, most of the set of tools, templates and documents from Stradivari's workshop went to his heir, and after a well-known sequence of owners and keepers, is now at the *Museo del Violino* in Cremona (Italy) [16].

Only a small number of Stradivari's artefacts were sold to a travelling violin dealer named Luigi Tarisio (*ca.*1790-1854) by their custodian Carlo Carli, who was in charge of Cozio's business affairs, shortly after Cozio's death. Among these artefacts the presence of six inner

wooden forms to make instruments (three for cello-size instruments and three for violin-sized instruments) is ascertained from the little-detailed surviving documents, and smaller items, including a rectangular-shaped ruler, are also mentioned [17,18]. This small subset of Stradivari's artefacts then went from Tarisio to the Parisian violin maker Jean Baptiste Vuillaume (1798-1875), and it was purchased in 1880 at the auctions selling the content of Vuillaume's workshop, for the *Musée du Conservatoire de Paris*, who later became the *Musée de la musique*.

The ink inscriptions on the set now in the *Museo del Violino* (Cremona set) were studied by a graphological and paleographical approach [19], allowing for the identification of writings by four different persons: Antonio, Francesco and Omobono Stradivari, as well as Cozio of Salabue. X-ray fluorescence spot analyses of the inscriptions on some of these artefacts indicated variations in the ink compositions [20].

The inscriptions on the artefacts now in the Paris *Musée de la musique* (Table 1) (Paris set) also consist of words, numbers, capital letters, a part of which were described [21]. But most of the artefacts of this set were not even described. From the provenance history of these artefacts, the most probable authors of these inscriptions are Antonio, Francesco and Omobono Stradivari, as well as Cozio of Salabue and Jean Baptiste Vuillaume. A compositional study of the inks may help discriminating these inscriptions into different groups.

TABLE 1. Diversity and number of inscriptions on the artefacts.

Type	Number	Artefacts where observed
Capital letter	23	E.901.3, E.901.4, E.901.6, E.903.12-14, E.903.16-18
Number	10	E.901.2, E.901.4
Date / Year	3	E.901.2, E.903.13, E.903.15
Word	10	E.901.1, E.901.2, E.901.4, E.901.5, E.903.13, E.903.15, E.903.18
Line	3	E.901.1, E.901.4, E.901.5

3. METHODS

3.1. Analytical technique

X-ray fluorescence (XRF) cartographies were performed using the M6 Jetstream instrument (Bruker) [22] containing a X-ray tube with a rhodium anode at 50 kV and 600 μ A with a 100 μ m thick beryllium window. Polycapillary optics are used to focus the X-ray beam. The X-ray detector is a 60 mm² SDD with a Peltier cooler, which 4096 channels were divided into 40 keV with a maximum count rate of 275 kcps. The target was placed horizontally at a working distance of 12 mm. The beam presented a diameter of 100 μ m, the distance between each point was 100 μ m and the time per point 200 ms. Data were processed with the Esprit program developed by Bruker. Current limitations of this software did not allow accessing the variability of individual spectra in a selected area of interest. Therefore, the calculation of statistical features within an area, such as standard deviation or margins of error was not possible in this environment.

3.2. Imaging to improve readability

Many inscriptions are today barely readable: some of them have suffered water damages, other have darkened (wood oxidation...), are covered with dirt, or the ink itself is degraded. The resulting lower contrast and elevated surface diffusion leads to poor readability of the inscriptions under visible light. Furthermore, superficial dirt often prevents from efficient reading under UV light. Elemental imaging raised the image contrast which was here based on elemental concentrations (Figure 2). The shape of the written signs (letters or digits) was thus better defined. It obviously was of interest for further eventual graphological studies but it was especially interesting here to better localize and select most appropriate areas for chemical analyses.

3.3. Imaging for quantification

In order to assess the protocol chosen to study the corpus of inscriptions, XRF single-point analyses were firstly performed and compared to the potential of the addition of numerous spectra extracted from the "datacube" obtained by XRF cartography. Three single-point spectra and one 1400-pixels sum spectrum acquired on one of the inscriptions — a capital letter — were compared (Figure 3). The metallic elements detected in inks were iron, copper and zinc, considered in this study as characteristic

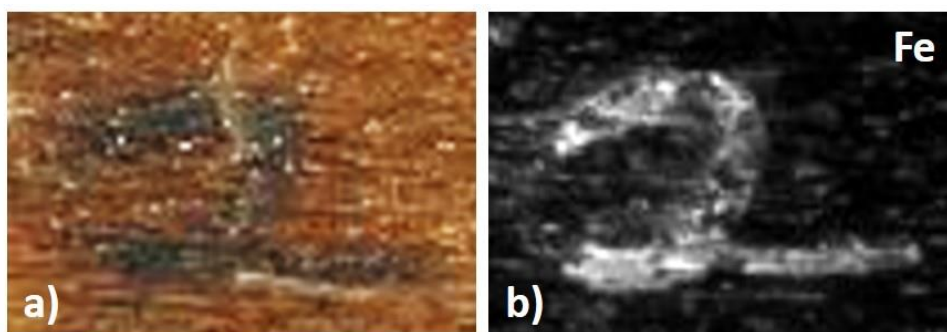


FIGURE 2. a) Visible picture of a detail of an inscription (artefact E.901.2); b) XRF cartography showing in white the distribution of the K α line of iron in (a).

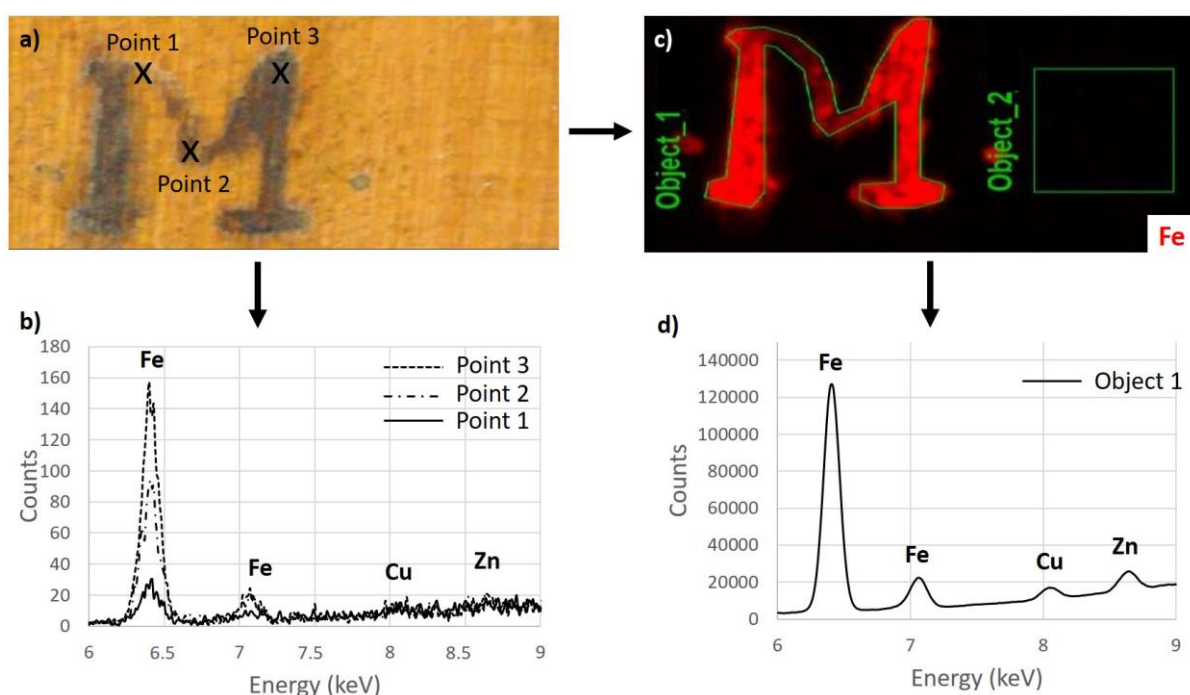


FIGURE 3. a) Visible picture of a detail of an inscription on the artefact E.903.18 showing the localization of the three single-point XRF analyses; b) XRF spectra extracted from the three positions in (a) centred on the K lines of iron, copper and zinc; c) XRF cartography of the K α line of iron showing the 1400 pixels area on the ink (Object_1) and the corresponding one on the wood (Object_2); d) Sum spectrum extracted from the Object_1 in (c). XRF, X-ray fluorescence

markers of the metallic salt used in the preparation of the ink. The single-point spectra showed notable differences in the intensity of the iron peak, which is due to the heterogeneity of the writing. Moreover, on some inscriptions, such as the one shown on Figure 3, the copper and zinc peaks were barely detectable. Therefore the representativeness of these single points analyses on a heterogeneous inscription was an issue, and with the poor signal/noise ratio of the three spectra, the error made on the elemental contents measurements was significant. Adding the signal of numerous pixels (Figure 3d) raised the signal/noise ratio.

It made the measurement more representative of the whole composition, thus improving the reliability of the quantification, which is a key point of ink discrimination.

It was chosen, for each inscription, to generate optimized areas of interest from the distribution of iron (the main metallic element) obtained by XRF cartography. All areas of interest had been designed to contain the same number of spectra: 1400. Given the experimental parameters, this number of spectra was well adapted to the diversity of sizes among the corpus of inscriptions. It corresponds to an analysed surface of $1400 \times \pi \times 50^2 \mu\text{m}^2 \approx 11 \text{ mm}^2$.

The wood substrates also contained small concentrations of iron, zinc and copper and these elements were heterogeneously distributed in the matrix at the scale of the beam spot: in average, spectra from inked-areas showed 9.6 times more iron, 5.4 times more copper and 4.3 times more zinc than the ones from the wood substrate. Thus, for each item the correction for the substrate was performed by subtracting the average sum spectrum of five 1400-pixels surrounding non-inked areas to the sum spectrum of the corresponding inked area. Margins of error corresponded to relative standard deviation estimated on a set of five 1400-pixels sums recorded on different non-inked areas near to the ink line.

The ink is supposed to coat the substrate in a thin layer of a few tens of microns. This geometry was favourable to apply, after subtracting the signal issued from the substrate, the approximation of a thin target for the determination of elemental contents. To convert the net area of peaks into concentration, model samples were used. Three series of model samples were prepared, consisting of Whatman

4. COMPARISON OF INKS COMPOSITION

Iron, copper and zinc, were quantified in all inscriptions of the corpus. In some rare cases, only two of these three metals were present, as for the inscription on the back of artefact E.901.1 where no zinc was detected.

The concentrations obtained were then gathered and compared keeping in mind that the ink could be deposited in different quantities from one inscription to another. Absolute concentration values were therefore much less

papers impregnated with iron, copper or zinc by immersion in respectively $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ or $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solutions during 10 minutes. Whatman papers were thin enough to neglect incident and emitted beam absorption phenomena. Model samples were thus considered as thin targets. For the iron set presented here as an example, concentrations ranged from 0.05 to 209 $\mu\text{g}/\text{cm}^2$ (Figure 4a). All model samples were analyzed by XRF under the same conditions as the inscriptions (Figure 4b). The spectrum of an area of 1400 pixels for each concentration was fitted in order to extract the net area of the $\text{K}\alpha$ line peak of each element leading to one calibration curve per main element (Figure 4c).

Whatman paper used for these model samples originally contained 5 ppm of iron, 1.2 ppm of copper and 2.4 ppm of zinc according to the supplier. These original concentrations introduced a bias in the standard curve so that the line did not pass through the origin. To calculate the concentrations of the elements in the ink of the inscriptions, only the slope of the line was then considered.

informative than correlations between metals. Concentration of iron obtained for each inscription was plotted as a function of the one of copper (Figure 5a) and zinc (Figure 5b). Linear correlation sometimes appeared between these elemental contents suggesting similar proportions in metals and thus a common origin of the elements. At this stage, it should be kept in mind that a difference in metallic proportions necessarily means the use of different inks, whereas similar proportions only means the use of a similar vitriol for the making of the inks.

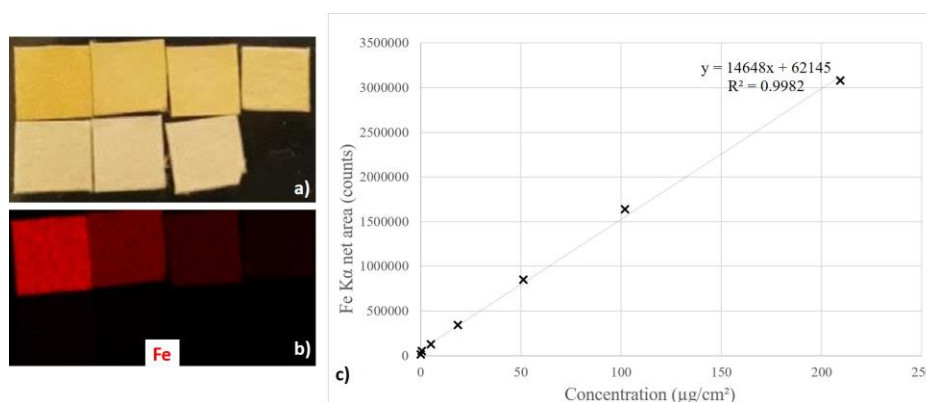


FIGURE 4. a) Visible picture of model samples made of paper test chart soaked in a solution of FeSO_4 at (from top left to bottom right) 100, 50, 25, 10, 2.5, 0.25 and 0.025 $\text{g} \cdot \text{L}^{-1}$; b) XRF map of the samples in (a) showing in red the distribution of the $\text{K}\alpha$ line of iron; c) Calibration curve made from the net area of the peak of the $\text{K}\alpha$ line of iron in the XRF spectrum as a function of the concentration of this element in the corresponding model sample.

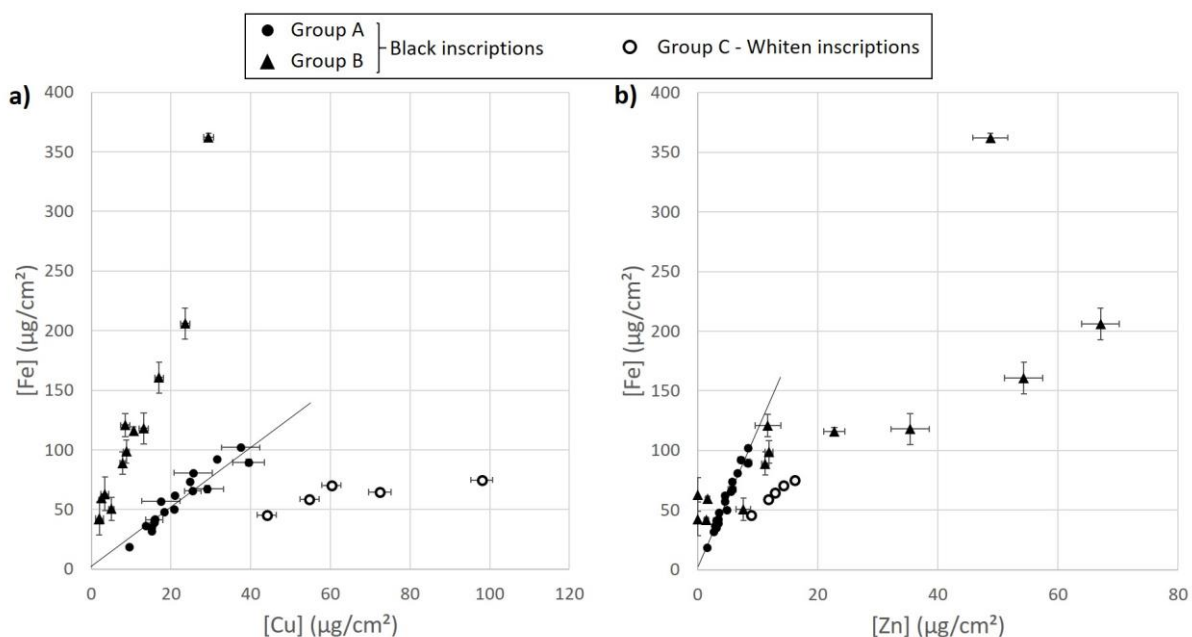


FIGURE 5. Iron concentration as a function of (a) copper and (b) zinc concentrations in the inks of all inscriptions of the corpus. Black dots correspond to black inscriptions and white dots to inscriptions showing a white layer on their surface.

The figure 5 shows that a large group of inscriptions (group A: black dots) followed a linear correlation between iron and copper and iron and zinc. All these inscriptions, belonging to five artefacts, were surely written with inks made of the same vitriol or, possibly, with the same ink. Additional historical information should be crosschecked with these data to go further in conclusions.

The figure 5 shows another group of inscriptions (group B: black triangles) that had a relatively low content of copper. The interpretation of this group was more delicate because the data were more dispersed (especially for zinc and iron) and because the corresponding linear regression did not go through the ordinate origin. For this group of data, the wood substrate itself was much richer in iron than for the previous group, thus jeopardizing the precision of the data when subtracting the signal of the substrate. This may contribute to the poor correlations of the data in this second group. Another explanation could be the use of different inks.

Finally, a last group of inscriptions (group C: white dots) had copper concentrations above $40 \mu\text{g}/\text{cm}^2$ with little scattering. However, their linear regression did not show convincing correlation.

Whereas all other inscriptions looked black (Figure 6a), the ones of the group C had a common visual whitish aspect (Figure 6b). Raman analyses were performed on these white layers using a spectrometer equipped with a microscope (Renishaw Invia, laser 785 nm , objective $\times 50$, power at 1.04 mW , grating of 1200 lines/mm for a resolution of 1 cm^{-1} , spot size $2 \mu\text{m}^2$, 50 accumulations, exposure time 5 s , range $500\text{--}1600 \text{ cm}^{-1}$). Two peaks were detected at 1005 and 982 cm^{-1} , corresponding respectively to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$). Precipitation of iron and calcium sulphates in the inks has already been reported in a previous work [23] and may correspond to the fact that the ink recipe contains originally a large quantity of iron sulphates and little binder (gum arabic). The phases obviously change the topography of the ink layer and the distribution of elemental contents. The stratigraphic structure of the writing induced by crystalline growth made the thin target approximation used for quantitative analysis non valid for the group C. Thus, further interpretations of the data obtained for this group would be conjectural.

Another way to consider the data was to plot the ratios Cu/Fe versus Zn/Fe (Figure 7). Indeed these ratios can be considered as reliable

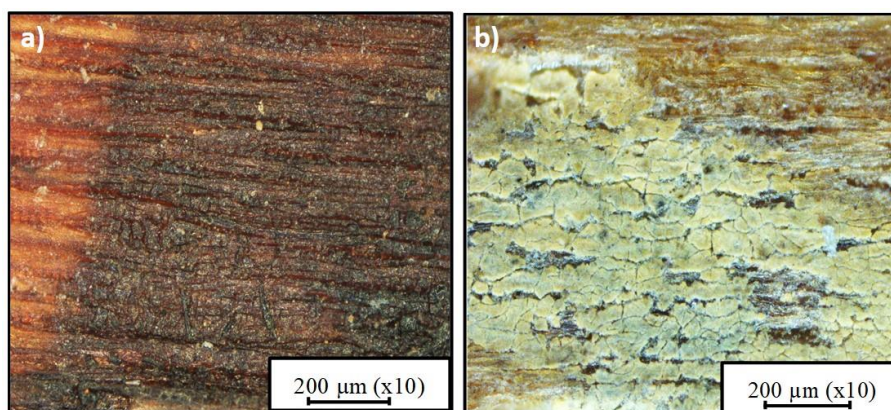


FIGURE 6. a) black ink (artefact E.903.12) and (b) whiten inscription (artefact E.903.15) as observed under visible light microscopy.

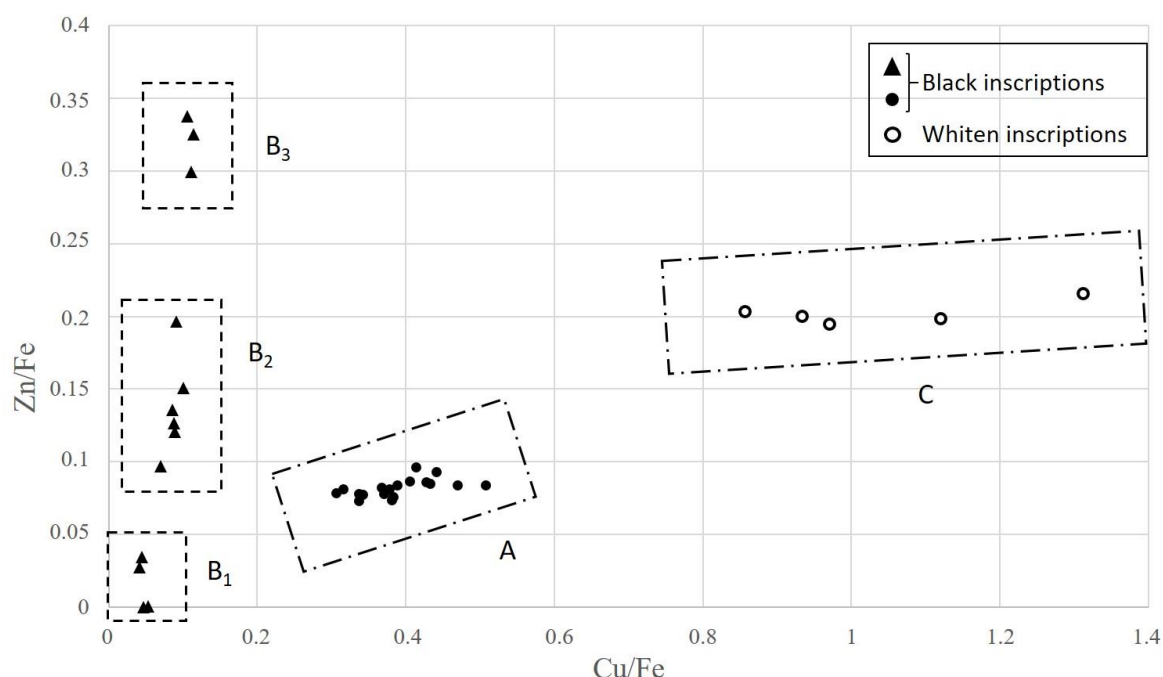


FIGURE 7. Mass ratio Zn/Fe as a function of Cu/Fe in the ink of all the inscriptions visible on the artefacts of the corpus. Black dots and triangles correspond to black inscriptions and white dots to inscriptions showing a white layer on their surface.

signatures of the composition of the vitriol used in the preparation of the ink. This representation allowed discriminating the three groups A, B and C already discussed above. Yet, group A appeared relatively gathered, whereas the two other were relatively scattered. Among the data of group B, three subgroups emerged, depending on the low, medium or high quantity of zinc (respectively B₁, B₂ and B₃). In the subgroup B₃, all inscriptions came from the same artefact, whereas for the others several artefacts were involved. Attributing a similar origin for the group B still remains highly conjectural.

5. IDENTIFYING THE AUTHOR(S) OF THE INSCRIPTIONS: A DISCUSSION

Elemental quantification of the metallic composition of the ink is a powerful tool to highlight analogies and differences but interpretation of these data should be done with great care. Many aspects could have a strong impact on the composition of the ink: first the ink pot itself, may be made of a metallic alloy containing copper. Since the ink can be highly acidic, some alteration of the container may occur, leading to the release of metals in solution. This has probably no significant

impact on the concentration of major elements, but it may affect the values of minor elements, such as copper in the case of group B. Then, the microstructure of the wood substrate includes various vessels and openings in which the ink may diffuse before its drying, having an effect on the homogeneity of the ink at the surface. Finally, each item has its own history and some of them were obviously subjected to abrasion of the surfaces or water damage, which may have significantly changed their elemental composition, as the inks are mostly on the wood surface and partially water soluble [24,25].

Elemental measurements alone are thus clearly insufficient for authenticating an inscription or stating the hand that held the quill. Crosschecking these data with any other possible information is the least caution to take. Graphology is for instance a complementary approach, which has already been applied to the complementary set of Stradivari's artefacts in the *Museo del Violino* in Cremona. Some writers among all the owners of the artefacts were identified as the authors of the considered inscriptions [19]. Inscriptions from this set were compared to the ones housed in Paris and some similarities arose. Indeed, some capital letters, dates and words show in both sets comparable styles of writings. Considering the chemical composition of these specific inks brought a new light on these considerations, sometimes confirming the analogies. Two inscriptions with different potential authors could show similar proportions of metals and, conversely, two inscriptions of the same potential author might show different proportions of these elements. These apparent contradictions find their explanations in writing habits that are determinant. Inkpots and quills could be shared between different persons. We know that Antonio, Francesco and Omobono Stradivari were working during four decades in the same space. They probably have soaked their quill in the same inkpot. Also, during the lifespan of the workshop, they had to replenish their supplies of ink, inducing a certain variation in the chemical composition of their inscriptions with time. These considerations not only stand for Antonio, Francesco and Omobono Stradivari, but also for all the owners of the artefacts.

6. CONCLUSION

The diversity of the inks used to write on artefacts from Stradivari's workshop was studied using X-ray fluorescence (XRF)

imaging spectroscopy. Spectral data extracted from XRF chemical maps were processed in order to improve the evaluation of the elemental composition of iron-gall ink inscriptions. In addition, the quantitative calibration of the system based on the thin target approximation allowed calculating the concentration of iron, copper and zinc and discriminating several groups among these inscriptions. This study showed the interest of this protocol to improve the representativeness of the spectra obtained by XRF and to raise the signal/noise ratio. Indeed, the selection of areas of interest made it possible to get rid of the heterogeneity of the ink of the inscriptions. Imaging techniques also provided the possibility of increasing the readability of the inscriptions and reconsidering some information present on historical objects.

A complete graphological study of the objects coming from Stradivari's workshop could complete the comparison with the artefacts present in the Cremona set to go further on the provenance of these inscriptions.

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