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Non invasive analysis of manuscript covers: portable X-ray fluorescence enlightening medieval jewellery masterpieces

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Abstract

This paper will present portable X-ray fluorescence (pXRF) analysis applied in situ to three 11th- 12th century manuscripts covers considered as masterpieces of Northern Italy medieval jewellery: Pace di Ariberto (Milano), Liber Evangeliorium of Vercelli and Pace di Chiavenna. These objects show a sumptuous decoration of golden leaves, plates and filigrees, enamels and casted gems. The aim of this research is to obtain information on manufacturing techniques and composition of the artefacts, considering possible analogies and differences that may be useful for art historians' discussion on manufacture place and artistic connections. XRF analysis was performed in order to determine the composition of the metals and enamels, and quantitative results, obtained using certified standards, undergo data treatment with multivariate analysis. The present paper will present a part of the results obtained on both the metals and glass materials, underlying the potential of pXRF in producing reliable results also when working in non-ideal conditions.

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Keywords: XRF, medieval manuscript covers, enamels, portable X-ray fluorescence

1. Introduction

Medieval manuscripts are well known as precious works of art thanks to the presence of charming miniatures and illustrations, sophisticated lettering and layout. The outer side of the manuscript, the cover, was often an essential element too, worthily fitting the status of work of art. Many medieval covers were in fact produced with

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precious materials, such as gold and silver, lushly laboured with filigrees, embossing and enriched with precious stones and enamels. The splendour and richness of the decorations were evidently connected to a particular use, for example during important celebrations for liturgical manuscripts, or to an important possessor.

Especially in the North of Italy, few of these outstanding covers are left, an analytical characterization of these works of art becoming indispensable in order to obtain information on their manufacturing technique and better understand their role in their geographical area.

Three of these covers, considered as masterpieces of Northern Italy medieval jewellery, Evangeliario di Ariberto (Milano), Liber Evangeliorium of Vercelli and Pace di Chiavenna, have been analysed in the contest of the MEMIP09 (Medieval Enamels, Metals and Ivories in Piedmont), a project focused on medieval works of art both in Piedmont and connected geographical areas.

This paper focuses on the results obtained with portable X-ray fluorescence (pXRF) analysis applied in situ on the metals and enamels, underlying the potential of pXRF in producing consistent results also when working in non-ideal conditions such as in situ analysis.

2. Materials and Methods

2.1. The covers

The three covers were originally created for an *Evangelistario*, a manuscript containing the passes from the Gospels to be read during the liturgy. The preciousness of the materials and decorations suggest that these objects were used during important celebrations such as *Pontificali* or during processions. The term "Pace", used for the covers of Ariberto and Chiavenna, refers in fact to those covers exposed to the people during liturgical processions, and then offered to the believers' kiss before receiving the sacrament. The golden valves show a sumptuous decoration of golden leaves, plates and filigrees. Casted gems and enamels, mainly of the cloisonné type, were used to create a suggestive and complex decoration. Two of the covers are composed of a second valve, which will not be discussed in this paper, since the main focus are the golden valves.

- The golden cover "Pace di Ariberto" is connected to the manuscript known as Evangeliario di Ariberto, commissioned by Ariberto di Intimiano, archbishop of Milan (1018-1045) for the Cathedral of Santa Maria Maggiore. The actual object, kept in the "Museo del Duomo di Milano", is a later manumission, which joined in a single binding the original silver cover and the lid of a box *–buchkasten-* produced some years later (1034-1036) to contain the manuscript [1].

- "Pace di Chiavenna" is the upper valve of an *Evangelistario,* now lost. It is part of the "Museo del Tesoro della colleggiata di San Lorenzo" in Chiavenna and the historical documents attest its presence in this area from 1486. No information on its manufacturing period, area or history is available. At present there are two hypotheses. The first is mainly based on the style of the enamels, and proposes a commission from the Emperor Ottone I, suggesting an oriental origin of the cover and an earlier production. The second hypothesis is based on the manufacturing technique and recognizes similarities with the school of Sant'Ambrogio altarpiece, suggesting a connection with the Milanese area and a production in the XI century. Moreover, the cover shows a significant manufacturing difference between the filigree of the external rounds and the central cross, which is more refined. For the central cross a later manufacturing has been proposed, dating to the 12th century [2].

- The manuscript cover of "Liber Evangeliorum" of Vercelli is composed of two valves, a silver and golden one. Its style refers to the Milanese school, however the manufacture of this object suggests a local production, possibly in Vercelli. The two valves are now conserved separately after the last conservative intervention in 2000, and according to the most recent hypothesis they were part of the same original binding produced in the 11th century. The golden valve shows an interesting symbolic and chromatic use of different alloys to obtain a peculiar coloristic effect and pointing out the importance of the enamels, brightly emerging from the background. Some manufacturing and style elements suggest that the whole cover was produced in Vercelli, which in fact was an important city and crossroads in the medieval era [3].

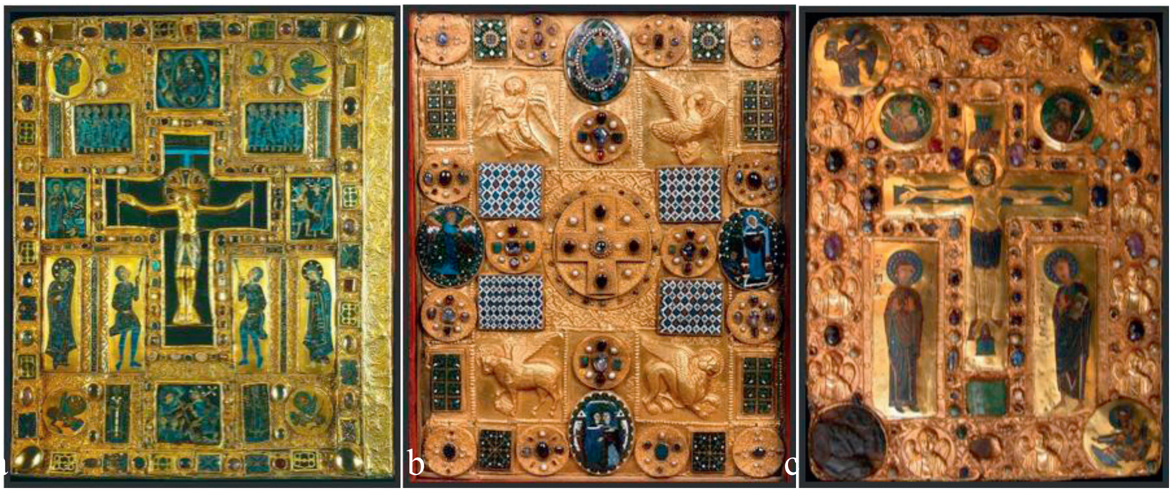


Fig. 1. (a) Pace di Ariberto; (b) Pace di Chiavenna; (c) Evageliario di Vercelli.

2.2. Instrumentation

The present study is based on Energy Dispersive X-ray fluorescence (EDXRF) [4,5] performed with portable instrumentation. The analyses have been carried out with two different instruments.

The first instrument is a modified Assing LITHOS 3000, with Mo target operating at 24 kV and 0,3 mA, Si PIN detector of 5 mm^2 with an energy resolution of 180 eV at Kα of Mn and shaping time of 6 μs. The geometry is 45°-52°, the ellipsoidal area hit by the beam being around 3 mm^2. The instrument is provided with a laser interpherometer in order to maintain the working distance constant to 9.4 mm. The analyses have been carried out for a live time of 300s, in air and helium. The lower detectable element is Si.

The second instrument is a commercial Thermo NITON XL3T GOLDD with Ag target, tension variable between 6-50 kV and maximum amperage of 100 μA. Each analysis consist of four different measurements: (LIGHT: 6 KV, no filter; LOW: 20 KV, Cu filter; MAIN: 40 KV, Fe-Al filter; HIGH: 50 KV, Mo filter). The detector is a Si Drift detector (SDD) of 25 mm^2 area. The geometry used is 30°/30°, with a working distance of 1 mm and a focal point of 3 mm of diameter. The analyses have been carried out for a total time of 120s for metals and 240s for the enamels. The analyses have been carried out in air, where the lower detectable element is Al also in very low quantities.

The obtained spectra have been processed with the commercial software package WinAxil, derived by the academic software IAEA [6]. Quantitative data was obtained using the software WinFund by means of Partial Least Square approach and a set of appropriate Certified Reference Materials (CRM). Part of the data processing has been pursued using Principal Components Analysis (PCA).

3. Results and Discussion

3.1. Metals

As explained above, one of the main issues about Pace di Chiavenna cover was the later manufacturing proposed for the central round, the hypothesis being founded on a different style and superior manufacturing ability. The possibility of a different manufacture could be proposed also based on the composition: the filigrees of the cross show in fact a different composition in respect to the external rounds (Fig. 2b), with lower Au and higher Cu and Ag content. However, a mechanical reason can explain this difference: the three level structure and the stones decoration are quite heavy, therefore the artisan may have decided for a more rigid structure lowering the Au content. It is important to underline that the backside sheets of the external rounds have the same composition as the sheets used as background in the cover, signifying that only the central cross has been threated differently. The integrations of the cover are a brass alloy for the substituted sheet under the enamels (Fig. 2c) and a Cu based alloy gilded with amalgam [7], the Hg contents indicates that the external gilded sheet should be anterior the XIX century.

Fig. 2. (a) Detail of Vercelli cover with the missing enamel of Saint Mark in the lower left corner; external round (b) and brass substitution (c) in Pace di Chiavenna.

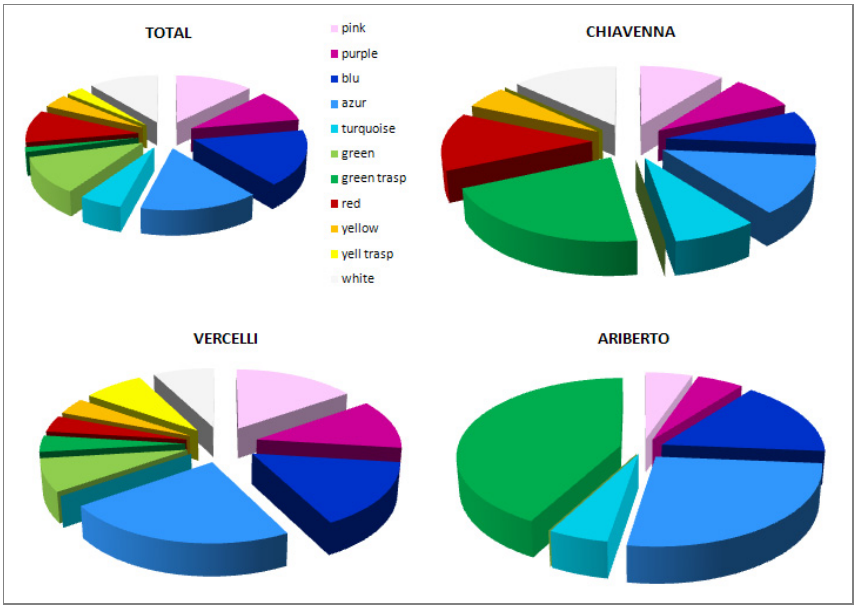
The results obtained on Vercelli cover indicate a chromatic use of the different alloys linked to the symbolic meaning of the subject [3]. It is possible to notice a variation of the three main elements, Au, Ag, Cu, in order to obtain the different color shades. The background and the filigrees are characterized by higher Cu content and a reddish shade color. The angels show higher Ag content and intermediate shade, while the high Au content of the plates produce a bright yellow color. In Vercelli cover the variation of the alloy composition is more relevant respect to Pace di Chiavenna. In fact, in Chiavenna the composition variation was likely due to mechanic reasons only, while in Vercelli cover the main purpose is the chromatic contrast between the different alloys.

However, the higher contents of the filigree in Cu respect to the background sheet has a technical reason: the alloy is harder and therefore, more resistant to physical damages. On the contrary, the plates of the enamels have a very high Au content and are therefore less hard, this required a mastic support in order to maintain them in shape, as it can be seen in the missing enamel. This expedient was not used for the rounds with the angels, which in fact show a number of cracks and collision marks (Fig. 2a).

Results on Pace di Ariberto confirmed that the integration of the sheet above St. Lucas enamel is a proper Au-Cu-Ag alloy and not a gilding. The analysis also confirmed that the black material used to delineate the hair of the Christ is *niello*, a particular substance obtained mixing Ag_2S and Cu_2S, with a theoretical ratio 2:1, according to manuscript Mappae Clavicula (XII century)[8]. The result on this spot has to be considered as semi-quantitative because of the presence of the underlying Au layer, and because of the error on evaluating sulphur. However, our result seems to indicate a much higher content of Ag respect to Cu.

3.2. Enamels

The analysed enamels cover a wide spectrum of colors, represented in Graph.1. Blue and green colors seems to be overrepresented, but in effect they are widely used in the covers; on the other side, some colors such as black, yellow and red are effectively underrepresented or missing because their area was too small to be analysed with a 3 mm diameter spot size. This is important to bear in mind in order to understand the constraints of this kind of objects where the high level of the manufacturing is often represented by the ability in producing smaller details.



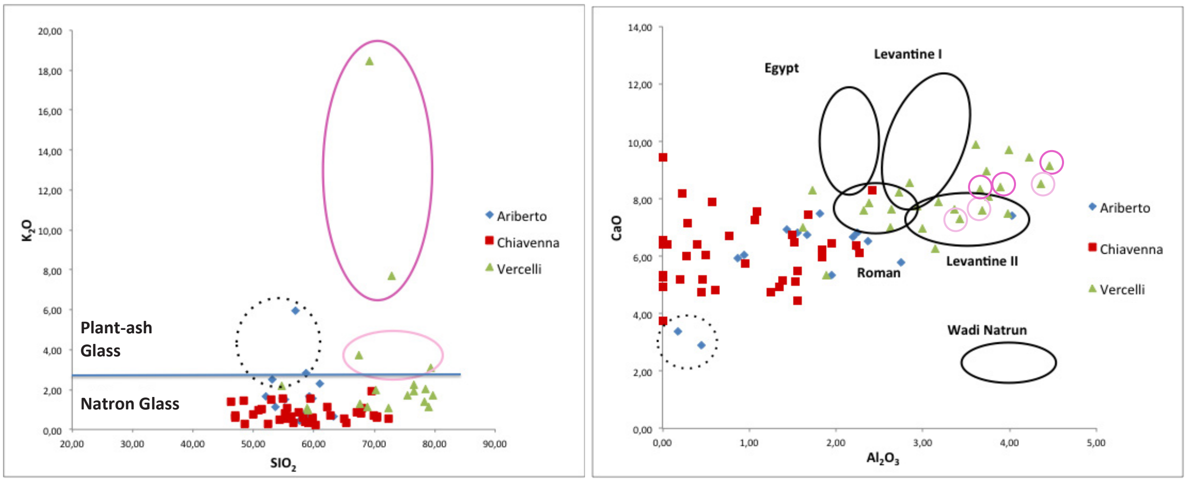
Graph. 1. Color occurrence in the total set of data and in the single covers of Chiavenna, Vercelli and Ariberto.

In this work, it is clear that a discussion of portable X-ray fluorescence analysis applied on glasses has to consider that lighter elements, such as Mg and Na, are undetectable by the instrument. The sum of their contributes is in fact called “dark matrix”, theoretically it can be obtained subtracting the sum of the detected elements respect to the total composition attended [4]. Assumptions have to be made very carefully, but some indirect evaluations can be made, for example about the Na presence on the basis of the K amount.

As reported in literature, typical Roman Na-glass is characterized by a total amount of K_2O and MgO lower than 1% with K_2O =0.75±0.24 and MgO= 0.6±0.3wt% [9] while soda plant ash glass is characterized by K_20 and MgO higher than 2.5 wt%. This value is represented by the horizontal line in the SiO_2 versus K_2O graph (Graph. 2a). The majority of data of the three covers has an intermediate composition in this range: this may indicate the matrix composition not to refer to a pure natron glass, possibly being instead recycled natron glass, whose practice was well know form the Roman period [10-11] with small amounts of a K-containing flux, both plant ash or wood-ash. Plant ash is known to appear from 9th-10th century in Northen Italy, such in Grado [11] or in venetian area [12].

The only exceptions are the purple glasses of Vercelli, showing K_2O content consistent with wood ash glass, the pink glasses whose shift is connected to the purple glass presence in the matrix, and finally, some later substitutions in Ariberto cover.

In the CaO versus Al_2O_3 graph (Graph. 2b), points tend to assest on intermediate CaO contents, while there is a wider dispersion on Al_2O_3, especially in Chiavenna. However, it is possible to observe that there is a partial overlapping of Chiavenna and Ariberto in the middle range while Vercelli is set on higher values, forming a group scattered along a linear relationship between the two elements. It is interesting to observe that the position of Vercelli purple enamels is on the extreme right of the cluster, together with the majority of transparent enamels. This specific fact and the correlation between CaO and Al_2O_3 could mean several things, one being the addition of a transparent glass producing intermediate compositions.

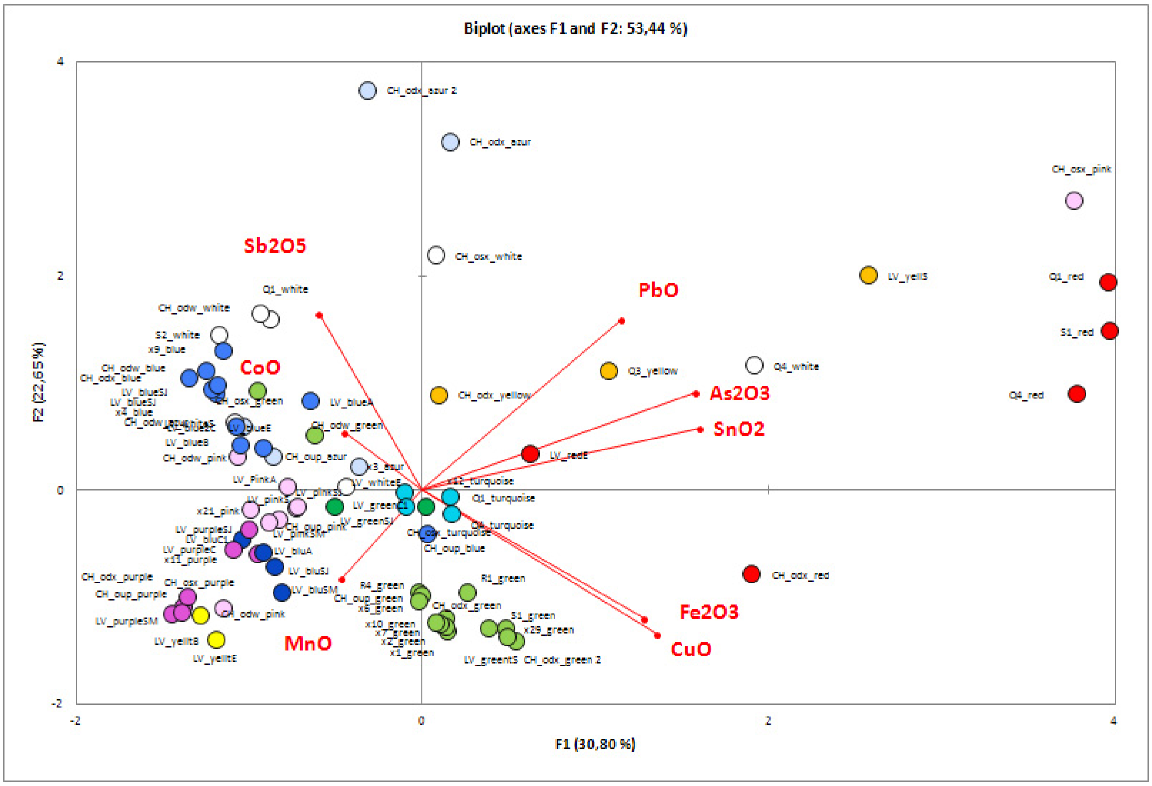


Graph. 2. Study of the matrix composition with binary diagrams, contents are expressed in wt%, dotted circle indicates the later substitutions in Ariberto. (a) SiO_2 versus K_2O graph: circles indicate purple and pink enamels in Vercelli, (b) CaO versus Al_2O_3.: the circles refer to the main types of glasses produced in the Antiquity as reported in (Fiori, Mazzotti e Vandini 2004).

Principal Component Analysis was performed on our set of data in order to evaluate the trend of the data of the three covers respect to the relationship between color shade and coloring agents (Graph. 3). The total variance of the PCA is low but it was enough to recognize out of chart data, detect some data clusters and interesting differences between the covers. The out of chart data were easily recognised because of very different compositions of the matrix as well as of the colorants contents and are not included in the PCA. An important observation before analysing the data is the macroscopic inhomogeneity of some enamels, especially the pink and the blue ones, for example the blue, light blue and turquoise shades, in St. Matthew aureole in Vercelli or in the Virgin Mary in Chiavenna, where the inhomogeneity lead to composition variations on the same color shade. For this reason too, the overall view of the PCA graph can allow a better comprehension of the situation respect to the comparison of the single weight percentages. For example, using the PCA to evaluate compositional variations in the same enamel area, such as abovementioned, allows to understand the effective significance of the data fluctuation of one single variable respect both to the observed data and the other variables. The general overview clearly has to include a cross-verification between PCA and weight percentages interpretation.

It is interesting to observe the presence of only one kind of opacifier, that is calcium antimonate ($Ca_2Sb_2O_7$), recognized by Ca and Sb. The only exception is the pink of the Angel's face in Chiavenna, where tin oxide (SnO_2) have been used. This is very interesting, because according to literature calcium antimonate was the usual Roman opacifier [13, 14], thought to be the only used until the 11th century as long as earlier evidence of tin oxide use was found in Italy, in a 6th-7th century site in Brescia [13]. We therefore have in the same enamel element two different opacifier, calcium antimonate used for the white, tin oxide only used for the pink.

The red enamels show a high Cu content and a very high Pb content, variable amounts of Sn and Sb, the last higher in Vercelli and As. The red color was therefore likely obtained with Cuprite particles (Cu_2O) dispersed as particles in a glassy phase with Pb, while the glass has possibly undergone cooling in reducing atmosphere [14]. Sn was possibly added together with Pb through metal alloys containing both the elements.



Graph. 3. Principal Components Analysis (PCA) of the enamels of the three covers: VC (Evangeliario di Vercelli), X (Pace di Ariberto), CH, Q, S (Pace di Chiavenna).

The opaque turquoise shade is obtained by Cu^{2+} dispersion in the glassy matrix, which should have undergone cooling in oxidizing atmosphere, with the addition of Sb as opacifier and low quantities of Pb [14]. Co traces where found in Chiavenna turquoise enamels, but it was possibly due to contamination from nearby blue Co colored glass.

The dark blue to light blue colors were obtained with Co and the addition of Sb in order to obtain the dark opaque blue and the lighter blue shades. It is interesting that in Vercelli we have both a transparent and an opaque dark blue, the first used on the Christ and the latter on the other images.

Pb and Sb content suggest lead antimonate both as colorant and opacifier in the opaque yellow glasses. Higher amounts of Mn are used as to reduce Fe(III) at Fe(II) and produce a pale yellow shade in the yellow transparent glasses in Vercelli.

The transparent green enamels show high Cu content associated with the Fe amount. The green opaque glasses in Vercelli were instead obtained with Cu present as Cu^{2+}, responsible for a blue-turquoise color, together with lead antimonate dispersed in the matrix as yellow particles and therefore resulting in a green opaque color [15].

Purple glasses are obtained with Mn dispersed as ion Mn(IV) in the matrix such as reported in literature [14] while the pink are always obtained with Sb addition, and sporadic presence of Sn. The only exception, as already stated above, is the pink of the Angel in Chiavenna, where it was used Sn.

With respect to minor elements, we observed a clear relationship of purple glasses and Ba content in Vercelli cover, where they are correlated to the K amount, and not to the colorant neither to Ca values. This would suggest a source of Ba in or with the flux source, this topic still being under discussion. Also, Rb content is related to K_2O, with considerable quantities in purple glasses linked to the high contents in K_2O [16].

3.3. Conclusions

The analysis campaign on the golden valves of Pace di Chiavenna, Pace di Ariberto and Vercelli Ligature allowed obtaining a wide range of information on both the metals and enamels using the XRF technique with a portable instrument.

The quantitative analysis on metal alloys could reveal interesting aspects for the comprehension on the manufacture. The different composition of the central cross and the external rounds of Chiavenna is of relevant interest, as it can be explained both with a choice based upon mechanical properties of the materials, both because of a later production of the central cross .

The enamels analysis allowed determination of the composition of the majority of the color shades, confirming some later substitutions and opening some interesting issue about the pink obtained with Sn in Chiavenna and the hypothesis of the coexistence of two different kind of glass matrix in Vercelli enamels. In general, the composition of the enamels suggested a similarity between Chiavenna and Ariberto and a completely different production for Vercelli. The hypothesis of a recycling procedure and the addition of a transparent glass were taken into account for the last cover, which evidently will require further analysis to be discussed properly. This last result is important not only because of the possible implications in the study of Vercelli cover, but it is significant also because it was obtained using a portable instrumentation despite the lack of information on Mg, Na and P.

The portable XRF technique was therefore confirmed as a valid tool for the comprehension and the study of complex materials. Despite intrinsic limitation of the portable instrumentation, which however are more an more being overcome thanks to exponentials advances in detectors, results were obtained both on metals and enamels, advanced hypotheses being also made on the glass matrix. About this topic, invasive analysis to perform a more complete and full wide study of the matrix and colorants function would be suggested, but strictly limiting the sampling to actual points of interest thanks to portable XRF previous contribute.

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