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Characterisation of the different hands in the composition of a 14th century breviary by means of portable XRF analysis and complementary techniques

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Abstract: A 14th century breviary known as *Breviario di San Michele della Chiusa*, produced at the disposal of the monks of Sacra di San Michele abbey (near Turin, Italy) has been analysed in order to identify the different authors who contributed in its making. The study aimed at revealing how many scribes composed the text and the musical notations and how many artists worked for miniatures and for the decorations of initials. All inks and decorative features have been analysed by means of portable XRF spectrometry for determining elemental distribution and by means of UV-Visible diffuse reflectance spectrophotometry with optic fibres (FORS) and spectrofluorimetry for identifying colourants. The results on non-invasive measurements highlighted that at least 11 persons (6 scribes for the text, 2 scribes for the musical notations, 2 artists for initials and filigrees, 1 artist for the full-page miniature at f. 208v) were at work at the *Breviario*. Moreover, the black inks used for text and notes have an anomalous composition, being irongall inks with a larger than usual amount of zinc, possibly as a consequence of the use of vitriols made from goslarite; this suggests that the scribes could come from Northern Europe.

Keywords: manuscript; inks; non-invasive; XRF; goslarite

1 Introduction

The contributions of analytical chemistry to cultural heritage can be highly variegated, ranging from authenticating artworks or archaeological remains to identifying the geographic provenance of an item. One fascinating aspect is the identification of different hands in an artwork, i.e. the different authors who contributed in its creation. This can be revealed if authors used materials that can be someway distinguished: an example is the palette used in a painting.[1,2] The identification of different hands provides useful information for a thorough comprehension of the artwork, such its meaning and symbolic value, its conservation and restoration history, etc.

Items that may be created from different contributions are typically the manuscripts. In the Middle Ages, in the creation of a manuscript inside a scriptorium it was common practice dividing the whole of the writing among different scribes,[3] in order to speed up the procedure; all sections were then unified by another artisan specialised in bookbinding. Usually, scribes were designated for writing only, while other artisans, more skilful in painting or drawing, were designated for miniatures, decorated initials and other artistic features. In the case of musical texts such as antiphonaries or breviaries, it was possible that some scribes contributed for text while other scribes contributed for the musical notation.[4]

While it is not generally difficult to identify different contributions in a painting, according to the different palettes present, it may be harder to distinguish among different scribes in a manuscript because it is highly probable that the same kind of ink had been used, especially if scribes worked inside the same scriptorium. With concern to black inks, in the Middle Ages manuscripts in Europe were mostly composed with the so-called iron-gall inks (IGI in the following) obtained from gallnuts.[5] The preparation of IGI involved milling gallnuts, extraction with water and addition of $FeSO_4$, known as *vitriolum romanum* (Roman vitriol), and of other vitriols ($CuSO_4$, $ZnSO_4$), to form a soluble Fe^{2+}-tannins complex. Oxidation of Fe^{2+} to Fe^{3+} by air caused precipitation of the insoluble Fe^{3+}-tannins complex which, dispersed into gum Arabic or other ligand media, generated a brown-black substrate suitable for writing, with a much higher durability than carbon-based inks. Despite IGI could be prepared with innumerable variations with concern to ligand media and/or additives,[6] it is usually not possible distinguishing different recipes, especially when only non-invasive measurements are involved. Moreover, when texts from the same scriptorium or even from the same geographic or cultural area are considered, it is possible that the same recipe had been used for preparation of black ink. At the same time, though, it must be considered that scribes were used to prepare small amounts of inks, covering few days of writing; preparations were not done on industrial scale, so that from one batch of ink to the following there could be slight differences in the raw matters, depending on their availability. This statement is even truer when considering different scribes, each one preparing his own ink. In the end, therefore, one possibility of distinguishing different preparations of ink can/must rely on the distribution of metals contained in the raw matters, such as vitriols or additives, which can be present as main components (usually iron or copper) or as impurities (manganese, zinc, lead, nickel, etc.). It is obvious that such a task can be fulfilled only with elemental analysis; therefore, techniques such as XRF spectrometry have a key role in studies on inks.

Similar considerations can be drawn on inks of other colours, i.e. red, blue, etc. which are made from pigments: cinnabar, red ochre or red lead in the case of red inks, azurite or lapis lazuli for blue inks. Again, different preparations could involve different impurities and therefore characteristic metal distributions.

In the past, some works were carried out in the analysis of manuscripts that involved characterisation of the elemental distribution in inks. Particularly interesting were the studies of Giuntini *et al.* on Galileo's writings,[7] which allowed to reconstruct a time sequence in their making. Hahn *et al.*[8] analysed historical manuscripts and music compositions, again identifying time sequences in the writings. Aceto *et al.*[9] distinguished inks in the black and red text of the Vercelli Gospels, a 4th century manuscript reputed to be the oldest Gospels in Latin. Similar studies were performed on printing inks[10,11] that allowed identifying different artisans at work on Gutenberg bibles.

In this study, a 14th century breviary written on parchment and known as *Breviario di San Michele della Chiusa* has been analysed in order to identify the different authors who contributed in its making. The study aimed at revealing how many scribes composed the text and the musical notations and how many artists worked for miniatures and for the decorations of initials. All inks and decorative features have been analysed by means of portable XRF spectrometry for determining elemental distribution and by means of UV-Visible diffuse reflectance spectrophotometry with optic fibres (FORS) and spectrofluorimetry for identifying colourants.

2 Materials and methods

2.1 X-Ray Fluorescence spectrometry (XRF).

XRF measurements were performed with an EDXRF Thermo (Waltham, USA) NITON spectrometer XL3T-900 GOLDD model, equipped with an Ag tube (max. 50 kV, 100 µA, 2 W), a large area SDD detector, energy resolution of about 136 eV at 5.9 keV. Analysed spot had an average diameter of 3 mm and was focused by a CCD camera, with a working distance of 2 mm. Total time of analysis was 240s. The instrument is held in position with a moving stage allowing micrometric shifts, in order to reach the desired probe-to-sample distance; the stage is laid on a tripod. The obtained spectra have been processed with the commercial software WinAxil, derived by the academic software QXAS from IAEA.

2.2 UV-Visible diffuse reflectance spectrophotometry with optic fibres (FORS).

FORS analysis was performed with an Avantes (Apeldoorn, The Netherlands) AvaSpec-ULS2048XL-USB2 model spectrophotometer and an AvaLight-HAL-S-IND tungsten halogen light source; detector and light source were connected with fibre optic cables to an FCR-7UV200-2-1,5x100 probe. In this configuration, light is sent and retrieved with a single fibre bundle positioned at 45° with respect to the surface normal, in order not to include specular reflectance. The spectral range of the detector was 200-1160 nm; depending on the features of the monochromator (slit width 50 µm, grating of UA type with 300 lines/mm) and of the detector (2048 pixels), the best spectra resolution was 2.4 nm calculated as FWHM (Full Width at Half Maximum). Diffuse reflectance spectra of the samples were referenced against the WS-2 reference tile provided by Avantes and guaranteed to be reflective at 98% or more in the investigated spectral range. Blank correction was not efficient on both the extremes of the spectral range, therefore the regions 200-250 and 900-1160 were not considered in the discussion. The diameter of the investigated area on the sample was 1 mm. In all measurements the distance between the probe and the sample was kept constant at 1 mm. In order to visualise the investigated area on the sample, the probe contained a USB endoscope. The instrumental parameters were as follows: 10 ms integration time, 100 scans for a total acquisition time of 1.0 s for each spectrum. The system was managed by means of AvaSoft v. 8^{TM} dedicated software, running under Windows 7^{TM}.

2.3 Spectrofluorimetry.

An Ocean Optics (Dunedin, Florida, USA) Jaz model spectrophotometer was employed to record molecular fluorescence spectra. The instrument is equipped with a 365 nm Jaz-LED internal light source; a QF600-8-VIS/NIR fibre fluorescence probe is used to drive excitation light on the sample and to recover the emitted light. The spectrophotometer works in the range 191-886 nm; according to the features of the monochromator (200 µm slit width) and detector (2048 elements), the spectral resolution available is 7.6 nm calculated as FWHM. The investigated area on the sample is 1 mm in diameter. In all measurements the sample-to-probe distance was kept constant to 1 mm (corresponding to the focal length of the probe) with aid of a small black cylinder inserted on top of the probe, which also shields external light. Instrumental parameters were as follows: 2 s integration time, 3 scans for a total acquisition time of 6 s for every spectrum. The system is managed with SpectraSuite^{TM} software under Windows 7^{TM}.

2.4 Optical microscopy

A USB Dino-Lite (New Taipei City, Taiwan) AM4113T-FV2W model microscope was used to acquire digital images at 50x and 200x magnification ratios. The instrument is equipped with 375 nm and visible LED lights and a digital camera with 1.3 Megapixel resolution.

2.4 Multivariate analysis

Principal Component Analysis (PCA) was performed on XRF elemental data using XLSTAT (Addinsoft, Paris) v. 2012.2.02 software.

3 Results and discussion

The *Breviario* is datable to 1315 according to a precise notation inside it, and was composed in Northern Italy at the disposal of the monks of San Michele della Chiusa abbey, a well-known centre of spirituality still active at present, located in a mountain zone near Turin (Piedmont, Italy). It is composed by two books: the *Temporale*, i.e. a cycle of Sunday celebrations and of *Tempi Forti* of the year, and the *Santorale*, i.e. a calendar of Saints' feast days. Alongside the text, red and blue small initials are present, some simpler and some with much more elaborated filigrees. These last occur in red colour on blue initials, and in purple colour on red initials. A single, though highly relevant from the artistic point of view, full-page miniature is present at f. 208v, depicting Saint Michael fighting against a dragon.

The construction of the page architecture was done, as commonly in medieval manuscripts, by means of *rubricatura*, i.e. by tracing straight lines at definite intervals in order to mark the succession of writing lines. These lines, though very light, are still visible in the *Breviario* and were done with a tip lead (Pb) as demonstrated by XRF analysis at various points.

In the following discussion, results will be shown for the analysis of the black inks used for text and for notes, of the red, blue and purple pigments used for initials and decorations, and of the palette used for the miniature at f. 208v.

It is well known that x-ray sources can easily penetrate parchment (or paper as well) and cause fluorescence emission from the back side of the folio under analysis and from one or more underlying folios also, if they contain written/painted areas. Therefore, all XRF measurements were performed choosing areas that were free from ink or paint on the corresponding back side of the folio; moreover, to avoid contribution from the underlying folios, 10 cellulose acetate sheets were put below the folio under analysis in order to create thickness. Cellulose acetate was chosen as a material free from metals after checking it with a blank measurement. Finally, care was taken in avoiding areas that could have contributions from the opposite folio in case of loss of colour.

3.1 Black inks

All the black inks used for the *Breviario* for the writing, the musical notations and the text accompanying music, are of the IGI type as suggested by their FORS spectra (Figure 1). As all these inks appeared very dark, while usually IGIs appear brown or dark brown, a Raman analysis was performed *in situ* to verify the possible presence of carbon as an additive to IGI, but the hypothesis of an IGI/carbon mixed ink proved wrong as no trace of carbon was identified. Inks with a similar dark tone were noted on the text of the 8th century Insular manuscript *Lindisfarne Gospels*[12] but in that case also, no clear addition of carbon to IGI was highlighted. Therefore, Raman analysis confirmed that the black texts of the *Breviario* were written with a peculiar recipe made of pure IGI. Additionally, as it will be discussed later on, these inks are very peculiar in that they contain an unusually high amount of copper and zinc with respect to iron, while it is known from traditional sources that these inks were mostly prepared using mostly iron sulfate.[13-17]

3.1.1 Recognition of different hands in the text

According to the palaeographic studies by Notarrigo,[18,19] at least six different scribes worked at the *Breviario*, despite the fact that both volumes are graphically homogeneous, being written with a uniform gothic style known as *littera textualis*, This type of writing was developed in 13th and 14th century in France and England but later spread all over Western Europe.[20] The six scribes can be distinguished as follows, on a stylistic basis:

Scribe A - *Temporale* volume;
Scribe B - *Temporale* volume, text accompanying musical notations;
Scribe C - *Santorale* volume, first 20 *folia*
Scribe D - *Santorale* volume, *folio* 20 recto and verso, documentary lowercase cursive writing
Scribe E - *Santorale* volume, from 21 recto to the end of the volume
Scribe F - *Santorale* volume, text accompanying musical notations.

Scribes can in turn be divided into three groups, according to the variety of style:

1 - C, E and F hands: these scribes used a gothic librarian style of international effort;
2 - A and B hands: these scribes used a librarian writing very similar to *rotunda*;
3 - D hand: this scribe used a lowercase cursive writing.

Examples of letters from the six scribes may be seen in Figure 2. For each of the different sections, at least 6 points of analysis were executed by means of XRF spectrometry, determining the following elements: Al, Cu, Fe, K, Pb, S, Si and Zn; in addition, Ca, Cl, P, Sr and Ti were also identified but their signals were comparable to the signal arising from parchment, therefore they were not used in the comparison among different hands. All data, expressed as weigth percent (% w/w), were normalised to iron. A Principal Component Analysis (PCA) was performed on the dataset composed by 7 elements: Al, Cu, K, Pb, S, Si and Zn. The results of this investigation are shown in Figure 3 which reports the PC1 vs PC2 plot, accounting for 75.48% of the overall information. The classification is only partially coherent with the one proposed on palaeographic basis: it appears that hands E and F used similar inks, but hand C is very different from them. Hands A and B used inks not correlated as well, with A more similar to C and B more similar to D. The differences among inks in the various hands arise from raw sources, of course, with a major role given to vitriols, as it appears from the loadings plot superimposed to PC1 vs PC2 plot (Figure 3): the inks used by hands E and F have a higher content of Cu and Zn, while the inks used by hands B and D are poorer in vitriols other that Fe. A biplot showing the content of Cu and Zn normalised to iron (Figure 4) reinforces this classification.

The consequence of these results is the following: if, according to the palaeographic analysis, six different scribes were at work on the *Breviario*, it is reasonable to think that every scribe used his own ink, prepared according to a personal recipe; the alternative hypothesis of a common ink can be done only for scribes E and F.

It must be noted that a marked difference in the appearance of inks exists between the hair side (the side originally facing the animal's hair, generally recognisable by traces of hair follicles) and the flesh side (the side originally facing the animal's flesh) of folios: on the former side the text is darker and more clean, while on the latter side it is more faded (Figure 5). This difference, though, must not be attributed to different hands in the writing, but rather to the preparation of the parchment which was made according to the subalpine style;[21] this caused a stronger "hooking" of the ink to parchment on the hair side. XRF measurements confirmed that inks of the opposite sides of the same folio were absolutely identical in all instances.

3.1.2 Musical notations

Musical notations were made with IGIs appearing darker than those used for text. As for text, musical notations were not made by a single scribe: according to a palaeographic study,[22] at least two hands wrote them:

Scribe 1 - *Temporale* volume, ff. 86r – 93v, 244v-263r; *Santorale* volume, ff. 139r-145r, 191r-194v, 245v-254r, 265r-266v, 267r-279v;
Scribe 2 - *Santorale* volume, ff. 145v-151v, 254v-259v, 266v-267r, 288v-305r.

XRF analysis on notes highlighted again a significant difference between the two styles, as can be appreciated in Figure 6 (top) which shows the PC1 vs PC2 plot, accounting for 66.76% of the overall information; the same elements identified in text analysis, i.e. Al, Cu, K, Pb, S, Si and Zn, were used after normalisation to Fe. In this case the difference between the two hands seems more related to accompanying elements, such as Al, Si, K, than to the elements associated to vitriols, that is Cu and Zn; it is therefore probable that the two scribes assigned to the writing of music used similar recipes for what concerns the amount of vitriols, but with a difference in the additives.

Interestingly, the ink used for musical notations shows slight differences with respect both to the ink used for the main text and to that used for the text accompanying music. Using again PCA analysis on XRF dataset, from PC1 vs PC2 plot (Figure 6, bottom), accounting for 66.29% of the overall information, it seems like the inks used for music (scribes 1 and 2) have intermediate features between those of scribes A, B, C and D and those of scribes E and F. It is particularly noteworthy that the inks used by scribes B and F, respectively at work for the text accompanying music in the *Temporale* and the *Santorale* volume, are different from the inks used for the musical notations.

One can therefore hypothesise that different scribes were at work, a group writing text (scribes A, B, C, D, E and F), another smaller group writing music (scribes 1 and 2).

3.1.3 Comparison with other inks

The high contents of Zn and Cu in the black IGIs of the *Breviario* are somewhat unusual with respect to known data obtained on medieval manuscritps. In Middle Ages different kinds of vitriols were used, among which the so-called *vitriolum goslarensis* or German vitriol[23] which, apart from iron, was rich in zinc, being obtained mainly from the mineral goslarite, an eptahydrate zinc sulfate with formula $ZnSO_4{\cdot}7(H_2O)$ originally found in Rammelsberg mine, near Goslar (Niedersachsen, Germany). According to the scientific literature, IGIs rich in zinc could be more popular in Northern Europe, and perhaps archival research in the documentary sources of Hanseatic League could confirm this in terms of metals and vitriols marketed in the towns of Northern Europe. It is a fact that some analytical studies performed on manuscripts created beyond the Alps highlighted a significant amount of zinc besides iron in IGIs. Van Bos and Watteeuw[23] carried out a survey on illuminated manuscripts produced in the Low Countries in the range 11th-16th centuries, finding mostly Zn-rich IGIs. Similar results were found by Klockenkämper *et al.*[24] on a Flemish late 15th century manuscript and by Čechák *et al.* on documents of the Kingdom of Bohemia between 14th and 19th century.[25] Recently Wachowiak *et al.*[26] reported on the occurrence of inks with a percentage of zinc higher than iron in the 14th-century *Graduale de Tempore de Sanctis* held at Diocese Library in Pelplin (Poland); authors suggested that among the raw sources for these inks, a major role could be played by goslarite.

In rare cases the presence of goslarite has been signalled in Italian mines (Friuli Venezia Giulia, Sardinia, Trentino Alto Adige and Tuscany) but not in large amounts. Consequently, it is not surprising that most of the diagnostic information pertaining manuscripts produced in medieval Italy report only classical Fe-rich IGIs. In a work by Lucarelli and Mandò[27] on a group of documents written in Central Italy between 12th and 15th century, the trend of Cu/Fe ratio showed a raising of copper amount in the inks of later documents, as it was S/Fe ratio, so suggesting that other vitriols could be used in addition to $FeSO_4$; zinc was found at trace level on most documents except for a small series of manuscripts datable to the start of 15th century, whose Zn/Fe ratio was similar to the one found in the *Breviario*. Verri *et al*.[28] found high levels of zinc in the inks used for Italian drawings; these artworks, though, were datable to the Renaissance.

In order to evaluate the anomaly of the inks of the *Breviario*, a comparison was made with coeval manuscripts produced in the same abbey or in the same geographic area. It is known from literary sources that an active scriptorium was present at the San Michele della Chiusa abbey, which importance was acknowledged in particular in 11th century and later on in 14th century under the regency of abbot Guglielmo III di Savoia (1310-1325).[29] Unfortunately very few manuscripts from that scriptorium still remain to us, located at Biblioteca Nazionale Universitaria and other institutions in Turin, and most of them being just fragments used as bindings for more recent books. These remains could be identified thanks to stylistic features and/or to the lettering "secundum consuetudinem monasteri Sancti Michaelis de Clusa" ("according to the tradition of San Michele della Chiusa abbey"). Much richer is the heritage of documents on parchment, mostly kept at Archivio Arcivescovile in Turin. The comparison has been carried out against three categories:

1. manuscripts coeval to the *Breviario*, produced at the San Michele della Chiusa scriptorium: ms. RARI XIX.3 kept at Biblioteca Diocesana in Susa (Italy) and some fragments of liturgical books used as bindings of notarial files presently kept at Archivio di Stato in Turin; in addition, later manuscripts produced at the San Michele della Chiusa scriptorium (mss. D.VI.11 and E.VI.39, Biblioteca Nazionale Universitaria in Turin, 15th century) have been included in the comparison;
2. manuscripts coeval to the *Breviario*, produced in scriptoria located in Northwestern Italy (i.e. close to San Michele della Chiusa abbey) and presently kept at Biblioteca Nazionale Universitaria in Turin;
3. documents produced at San Michele della Chiusa abbey datable in a range of ± 16 years with respect to the *Breviario*, nowadays kept at Archivio Arcivescovile in Turin.

The black inks of all the books and documents involved in the study were analysed with XRF after verifying their nature as IGIs with FORS analysis. At least 5 points of analysis were determined on each item, verifying the homogeneity of inks along the whole text. The results of the comparison highlight the apparent anomaly of the black inks of the *Breviario*, as it is shown in Figure 7 which reports the PC1 vs PC2 plot, accounting for 74.45% of the overall information. The inks corresponding to A, C, E and F hands have elemental compositions far different from the other samples analysed; the discrimination is supported mostly by higher amounts of Cu, Pb and Zn as suggested by the loadings plot superimposed to PC1 vs PC2 plot (Figure 7). A biplot showing the content of Cu and Zn normalised to iron (Figure 8) confirms the clear distinction. As to the inks of B and D hands, these appear to follow more conventional recipes, being the amounts of vitriols similar to the other samples analysed.

The information arising from XRF analysis of the black inks of the *Breviario* allows us to formulate the following hypothesis: combining the palaeographic features of the writing and the differences in ink composition, it is possible not only that in the writing of the *Breviario* six different scribes were at work, but also that at least four of them (hands A, C, E and F) were external to the scriptorium of San Michele della Chiusa abbey, in agreement with the use of IGIs prepared largely from goslarite; the same holds true for the scribes who worked on musical notations. The hypothesis of foreign scribes was already cited by Notarrigo[19] with concern to A and B hands who could be related to scribes coming from Southern Italy, called at the abbey to offer their services; from XRF results it seems like this hypothesis should be extended to a larger number of scribes, if not to all of them. Alternatively, we must think of local scribes who were aware of the recipes used in Northern European scriptoria and were able to get themselves specific raw sources such as goslarite to produce their black inks. Finally, it must be considered that the abbey was placed inside a cross-border region with frequent contacts with French kingdoms (such as Burgundy), therefore with a high degree of exchange of techniques, materials and people.

To reinforce the above cited hypothesis about an external source or knowledge for black inks, it must be noted that the internal differences between A, C, E and F hands (and 1 and 2 hands for what concerns musical notations) are irrelevant if compared with the difference among the inks of the *Breviario* and the inks of all other manuscripts and documents taken into consideration in this study.

The use of a higher amount of zinc vitriol in ink could be explained with the role of Zn^{2+} ion as protective agent. Some studies[8,30] demonstrated that IGIs containing zinc were better preserved and had a darker tone, while IGIs rich in copper were more brownish and subject to alteration, most probably due to the catalytic effect of Cu^{2+} ion on the degradation of paper or parchment.[31]

3.2 Red initials and decorations

All red rubrics, initials and filigrees in the *Breviario* were made with cinnabar/vermillion (natural or synthetic HgS). As for the text, for decorated initials and filigrees also at least two different styles can be identified, the first one due to a hand elegant and attentive to details, while the second one due to a less expert and neat hand (examples in Figure 9 - a and b). This difference is confirmed by XRF analysis. At least 5 points were determined on red initials for each style, that yielded the results shown in Table 1; data are normalised to sulphur, being it a key element of cinnabar. For the comparison, the elements Cl, K, P, Pb, Si and Zn were taken into consideration, while Al, Sr, Cu and Fe, though determined, were discarded as their amounts were comparable to parchment. Apparently, the red pigment used by the less expert hand is richer in chlorine, lead and potassium, possibly as a result of the addition of a higher amount of white lead to cinnabar; in this case, the difference could arise from a different source of raw matters (e.g. lead and mercury minerals from different mines). Similar results were obtained from XRF analysis of the red filigrees that were used to decorate blue initials: the two different filigrees styles corresponded to two slightly different compositions of the pigment.

3.3 Blue initials

The case of blue initials is totally similar to red initials, i.e. two styles can be recognised suggesting different expertise (examples in Figure 9 - c and d). Both artists used azurite - $2CuCO_3 \cdot Cu(OH)_2$ - but XRF analysis highlighted (data in Table 1) that the less expert hand used the blue pigment more diluted with white lead; in this case elemental data were normalised to Cu, the key element for azurite. The elements used for the comparison were in this case Al, Fe, K, Pb and Si.

3.4 Purple filigrees

A large number of red initials were decorated with thin purple filigrees, which, according resulted to FORS and spectrofluorimetric analysis, resulted to be composed by folium, the dye extracted from C*hrozophora tinctoria* (L.) A. Juss. plant belonging to *Euphorbiaceae* family. The identification of folium is notable because this dye has been found on artworks in very rare instances.[32,33] Though *Chrozophora tinctoria* be a plant growing in warm and dry climates (e.g. Sardinia, Turkey, Southern France), the use of folium in a scriptorium set in a mountain zone is not surprising as this dye, like many others, was preserved in Middle Ages with the *pezzuola* method,[34] that is by soaking a linen clothlet into dye juice in order to make it absorb a relevant amount of dye, which could be later leached out with an alkaline treatment; in this way the clothlet would act as a portable reservoir for the dye. Also, it must be considered that the Sacra di San Michele abbey had properties in Southern France, so that *Chrozophora tinctoria* or folium itself could be easily recovered; in addition, being placed along the path between Mont Saint-Michel (Normandy, France) and San Michele Arcangelo (Puglia, Italy), the abbey could take advantage of cultural exchanges.

Upon visual inspection once again it is not difficult identifying two different hands in the making of purple filigrees: one less elaborate, characterised by wider strokes, and one highly sophisticated with thinner strokes and more evolved drawings (Figure 9 - e and f). In this case also, results of XRF analysis confirmed this distinction on the basis of the elemental composition of the inks used for the purple filigrees. It was not easy to decide how to normalise elemental data, because no apparent key element could be single out (folium is a dye, so it contains only light elements); therefore, it was decided to use raw data. K, P, Pb, S, Si, Sr and Zn were the elements used for the comparison. The results, shown in Table 1, once again confirm the hypothesis of two artists at work, each of which using his own folium solution; the ink used by the less elaborate hand is richer in lead, as if that ink was more diluted with white lead.

3.3 The miniature at f. 208v

It is interesting to evaluate whether the beautiful miniature at f. 208v, representing Saint Michael and a dragon (Figure 10), was composed by the same artists who worked at the initials or by another artist. According to analysis carried out by means of FORS, spectrofluorimetry and XRF spectrometry, the palette involved was composed by the following colourants:

- *red lead* for details depicted in orange such as the dragon's tail, vegetal shots, etc. (the same pigment is present in some tetragram lines mixed with cinnabar);
- *azurite* and *indigo* for blue details;
- *weld* for few yellow details (e.g. Saint Michael's shield); the presence of this dye was hypothesised on the basis of FORS and spectrofluorimetry analysis and of the fact that XRF analysis identified no key elements;
- *folium* for Saint Michael's dress and for details in the vegetation

Apart from the stylistic features, the whole palette suggests that another artist was at work in the miniature at f. 208v: the use of red lead in place of cinnabar can hardly be justified, considering that the latter pigment was widely used for rubrics, initials and filigrees all along the manuscript. XRF analysis of purple areas painted with folium highlighted a higher Pb amount with respect of the folium ink used for filigrees, but the comparison is in this case somewhat incorrect: it is logical to think that the purple paint in the miniature should have more hiding power than an ink, so more white lead could be needed.

4 Conclusions

The results on non-invasive measurements carried out on the *Breviario di San Michele della Chiusa* by means of XRF spectrometry, FORS and spectrofluorimetry, highlighted that at least 11 persons (6 scribes for the text, 2 scribes for the musical notations, 2 artists for initials and filigrees, 1 artist for the full-page miniature at f. 208v) were at work for writing and decorating it. Particularly relevant are the black inks used for text and notes which have an anomalous composition, being irongall inks with a larger than usual amount of zinc, possibly as a consequence of the use of vitriols made from goslarite; this suggests that the scribes could come from Northern Europe. As to the red/blue/purple colourants used for decoration, in all cases it was possible to distinguish between two artists according to the elemental distribution; this clear distinction allows us hypothesising that two scribes only were at work for both painting in miniatures and in filigrees, one more expert and the other less expert, as if a teacher and a student alternated in the decoration of the *Breviario*.

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Colour	Artist	Al	Cl	Cu	Fe	K	P	Pb	S	Si	Sr	Zn
Red initials	student	-	0,14	-	-	0,06	0,29	0,044	1	0,09	-	0,009
	master	-	0,02	-	-	0,01	0,39	0,003	1	0,05	-	0,010
Blue initials	student	0,03	-	1	0,037	0,01	-	0,010		0,953	-	-
	master	0,03	-	1	0,034	0,01	-	0,002		0,889	-	-
Red filigrees	student	-	0,18	-	-	0,05	0,25	0,040	1	0,08	-	0,008
	master	-	0,02	-	-	0,01	0,37	0,003	1	0,04	-	0,011
Purple filigrees	student	-	-	-	-	0,36	0,56	0,114	1,13	0,75	0,01	-
	master	-	-	-	-	0,29	0,97	0,022	1,66	0,54	0,005	-

Table 1 – Elemental compositions (% w/w) of red and blue initials and of red and purple filigrees in the *Breviario*

Figure captions

Figure 1. FORS spectra of black inks from the *Breviario*
Figure 2. Examples of letters from the six scribes of the *Breviario*
Figure 3. PC1 vs PC2 plot from elemental analysis of the black inks of the *Breviario*
Figure 4. Cu/Fe vs. Zn/Fe in the black inks of the *Breviario*
Figure 5. Text on the hair side (a) and on the flesh side (b) of a folio
Figure 6. PC1 vs PC2 plot from elemental analysis of the black inks of the musical notations of the *Breviario* (top); PC1 vs PC2 plot from elemental analysis of all black inks of the *Breviario* (bottom)
Figure 7. PC1 vs PC2 plot from elemental analysis of the black inks of the *Breviario* and of other manuscripts and documents
Figure 8. Cu/Fe vs. Zn/Fe in black inks of different manuscripts and documents
Figure 9. Different styles in red (a and b) and blue (c and d) initials and in purple (e and f) filigrees
Figure 10. The miniature at f. 208v, representing Saint Michael and the dragon