AN INTERDISCIPLINARY, NON-INVASIVE STUDY ON TEN MANUSCRIPTS COMING FROM THE SAN COLOMBANO ABBEY IN BOBBIO

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ABSTRACT
A group of ten manuscripts datable to the X century A.D. and coming from the S. Colombano abbey in Bobbio (Piacenza, Italy) were analysed with non-invasive techniques to characterise the ancient palette of the abbey scriptorium. All analyses were performed in situ using portable instrumentations. Raman spectroscopy, UV-visible reflectance spectrophotometry and XRF spectrometry were the techniques used. The advantage of using complementary techniques was well demonstrated by the nearly full characterisation of the palette of the manuscripts. Results obtained are interesting from different points of view: first at all, being these manuscripts already studied under the historical and artistic side, chemical analysis can give a strong support to the considerations of art historians; secondly, some conservation emergencies were identified that would need to be addressed, that is changing of minium to black plattnerite and tarnishing of copper, used as a substitute for gold, to a greenish carboxylate, possibly acetate-carbonate. Lastly, the occurrence of ultramarine blue on a manuscript should be seen as one of the first evidences of the use of this precious pigment in Medieval Europe.

INTRODUCTION
The abbey of St. Colombano in Bobbio (Piacenza, Italy) is located in an Apennine valley, on an important communication route among three Italian regions: Lombardy, Emilia-Romagna and Liguria (Figure 1). The abbey was founded in 613 A.D. by St. Colombano, an Irish monk arrived in Italy as a missionary.

Figure 1- Geographic position of Bobbio (Piacenza)

The abbey is an extraordinary example of monastic *scriptorium*, in that it maintained strict bounds with other European cultures, in particular Irish and French. The highest manuscript output of the abbey, occurring from the end of IX to late X century, happened to coincide with a period of political and social upset all over Europe, in which most of the monastic centres in the Carolingian Empire, after the cultural richness of the Charlemagne age, were in deep crisis as a consequence of the decline of the Empire. Being Bobbio located in an advantageous geographical position, sheltered from barbaric incursions, its *scriptorium* succeeded in keeping active for centuries. Under the guide of abbot Agilulfo, in X century the Bobbio *scriptorium* was greatly renewed, possibly with skilful illuminators from Padua. Decorations on manuscripts were inspired to the French-Insular style, marked by extreme elegance and strictly ornamental character. Examples of decorated initials are shown in Figure 2.

Figure 2- Examples of illuminated initials in manuscripts from Bobbio scriptorium

This period of great manuscript production lasted up to end of X century, after which a new dark age took place. At present, most of the librarian production from Bobbio is held between the National University Library in Turin and the Ambrosiana Library in Milan. Among these, a set of 10 illuminated manuscripts dating to IX-X century were selected for analysis: these documents are an important witness of the problematic period described before. Interest for chemical analysis on pigments is due to the following points:

- characterisation of the palette/palettes used by illuminators, putting into evidence later interventions
- comparison among data obtained from analysis and artistic-historical knowledge on the abbey and its age
- information about conservation state of the miniature paintings

In the present work the analytical characterisation of the palettes of the seven manuscripts from Bobbio is reported. The manuscripts are those held in the National University Library in Turin. Research will be implemented in the near future with analysis on the three lasting manuscripts held in the Ambrosiana Library in Milan to complete the whole set. Analysis has been performed with totally non-invasive spectroscopic techniques, applied *in situ* with portable instrumentations. The techniques were the following:

- UV-visible spectrophotometry in diffuse reflectance mode with fibre optics (from now on cited as FORS, Fibre Optics Reflectance Spectrophotometry): being fast and easy to use, this technique was applied as a preliminary tool to identify most of the pigments and to check for similar painted areas, i.e. areas obtained with the same pigment;
- XRF spectrometry: this technique was used to characterise metal pigments (es. gold foil, shell gold, etc.), to verify the presence of superimposed painted layers and to identify contaminants in pigments that could be used as markers for provenance of raw materials;
- Raman spectroscopy: this is the technique with the highest diagnostic power and it was used to confirm identification of pigments in uncertain cases.

EXPERIMENTAL SECTION

XRF Spectrometry

Measurements were carried out by means a portable XRF spectrometer equipped with a Mo X-ray tube (Oxford Inc. TF 3005) and a Si(Li) pin detector (Amptek Inc. XR-100 CR) with an active area of 5 mm^2 , a resolution of 149 eV at 5.9 keV and Peltier cooled to -10°C. Operating conditions were 24 KV and 300 μA for a spectrum collection time of 300 s. The instrument probe was located on a tripod allowing flexible positioning in the different situations met during the analysis sessions. The manuscript under analysis was laid on a book cradle (Figure 3); a polycarbonate plate was inserted below the sheet being examined to avoid penetration of x-rays up to the underlying sheet, which could result in confusing responses. Moreover, to avoid contribution from painted area on the reverse side of the sheet, careful selection of analytical zones was carried out. All analyses were performed keeping the sample-to-probe distance constant to 1 cm, to allow comparison of inorganic contaminants in different pigments. A total of 57 different points was analysed, including parchment to evaluate its contribution to metal content in painted areas.

Figure 3- XRF analysis on manuscript

UV-Visible Diffuse Reflectance Spectrophotometry (FORS)

FORS measurements were performed with an Ocean Optics (Dunedin, Florida, USA) USB2000 model portable spectrophotometer was used. The system is composed by a spectrophotometer with detector in the range 200-1100 nm, a PX-2 Pulsed Xenon Lamp as light source and two optical fibre bundles to convey lamp light on the sample and diffusely reflected light from sample to the detector; both bundles end up in the same probe, so that geometry of light irradiation/collection was 45°/-45° in order to avoid specular reflectance and collect diffuse reflectance only (see Figure 4). The system is managed by a notebook with dedicated software OOIBase32 in Windows XP environment. Measurements were performed

with 20 ms integration time and 500 accumulations; total acquisition time was therefore 10 seconds on each point of analysis. During analysis, manuscripts were laid on a book cradle and kept open at 90°. A total of 200 different points was analysed, including parchment to evaluate its contribution to reflectance in yellow painted areas.

Figure 4- FORS analysis on a manuscript

Raman Spectroscopy

An Horiba (Villeneuve d'Ascq, France) MicroHR model portable spectrometer was used to confirm identification suggested by the previous techniques. The modular system is composed by a MicroHR spectrometer with 1200 gr/mm grating, a Synapse model CCD detector with 1024x256 pixels, a Modular Head model analytical probe head containing both notch filter and edge filter and a video camera for visualisation of samples, a microscope objective (20x, 50x and 80x) held to probe head, a He-Ne laser (λ = 632.8 nm) with an output power of 20 mW reduced by attenuation filters to less than 1 mW on the sample and two optical fibre bundles to convey laser radiation on the sample and Raman scattered light from sample to the detector. With this optical configuration the spectral resolution was about 4 cm^{-1}.The system is managed by a notebook with dedicated software LabSpec 5 in Windows XP environment. Total accumulation time range from 1 to 30 seconds according to needs; longer times were not used in order to avoid the effect of wrinkling that is known to occur on parchment subjected to laser irradiation, causing loss of focus. During analysis, manuscripts were laid on a book cradle as shown in Figure 5. A total of 81 different points was analysed.

Figure 5- Raman analysis on manuscript

It is important to point out the fact that under no circumstance damage was caused to the manuscripts; moreover, none of the techniques used was even in contact with the painted surfaces upon analysis. The only requisite for analysis was to lay manuscripts in flat position and to apply light weights on the sheets being examined in order to limit the natural wrinkling of parchment. It was decided to avoid long periods of times for the manuscripts to stay open; for this reason, analysis time was limited to 2 hours per session on the same manuscript.

RESULTS AND DISCUSSION

It is noteworthy to state that these manuscripts have been thoroughly studied under the historical and artistic side (Cipolla, 1907; Crivello, 2001), so that chemical analysis can give a strong support to the framework based on the considerations of art historians. The manuscripts selected for analysis represent a set characterised by homogeneity of decorations and liturgical and hagiographical contents; there are stylistic differences. The manuscripts are listed in Table 1.

No.	Name of manuscript	Period	Code	Site*
I	*Gregorius Magnus, Moralia in Iob*	late IX century	F.I.6	NULT
II	*Lectionarium*		C. 228 inf.	ALM
III	*Missale Plenarium*	early X century	D 84 inf.	ALM
IV	*Homilarium*		F.II.19	NULT
V	*Psalterium*		G.V.2	NULT
VI	*Passionarium*	first half IX century	F.III.16	NULT
VII	*Homilarium*		F.II.20	NULT
VIII	*Ionas Bobiensis, Vita Columbani*		F.IV.12	NULT
IX	*Ionas Bobiensis, Vita Columbani*	X century	F.III.15	NULT
X	*Homilarium*	X century	E 20 inf.	ALM

Table 1 - List of analysed manuscripts from Bobbio
** NULT: National University Library, Turin; ALM: Ambrosiana Library, Milan*

Among this set, the manuscripts can be divided in four groups according to decoration styles:

- *Agigulfo group*, composed by manuscripts F.I.6 and C228 inf., the most valuable under the artistic point;
- *Messale group*, composed by manuscripts D84 inf., F.II.19 and G.V.2, slightly less valuable than the previous group
- *Vita Columbani group*, composed by manuscripts F.III.16, F.II.20, F.IV.12 and F.III.15; this group shows a stylistic gap with respect of the previous two, being miniatures much less accurate and rich in style;
- manuscript E20 inf. is stylistically different from all others

Development of Spectra Databases

In order to improve pigment identification, two databases of spectra of pigments on parchment were developed, one for Raman spectroscopy and one for FORS. A set of 65 pigments, dyes and lakes known to be used by medieval illuminators was selected; paints were prepared either as temperas in egg white and as watercolours in gum Arabic, following the original recipes reported in medieval art textbooks such as *De arte illuminandi* (Brunello, 1975) and *Il libro dell'arte* by Cennino Cennini (Frezzato, 2004); then painted areas were laid on parchment as shown in Figure 6. After drying, Raman and FORS spectra were collected to build corresponding databases. In this way a more accurate identification was reached on samples, being measurements carried out in almost the same conditions among samples (miniatures on manuscripts) and standards (paints laid on parchment).

Figure 6- Palette with medieval pigments, lakes and dyes on parchment

Characterisation of the Palettes

All painted areas of the seven manuscripts were analysed in a preliminary way with FORS. Reflectance spectra were then transformed in ASCII format to allow classification of painted areas with chemometrical techniques. Cluster analysis with Euclidean distance and Ward's method of agglomeration was applied to spectra of similar hues to put into evidence the use of different pigments. As an example, in Figure 7 a dendrogram resulting from cluster analysis of blue painted areas shows clearly the presence of three different pigments that can be identified as azurite (most probably XIV-XV century retouches), indigo (on the oldest manuscript) and ultramarine (on all other manuscripts). Raman and XRF measurements confirmed these identifications.

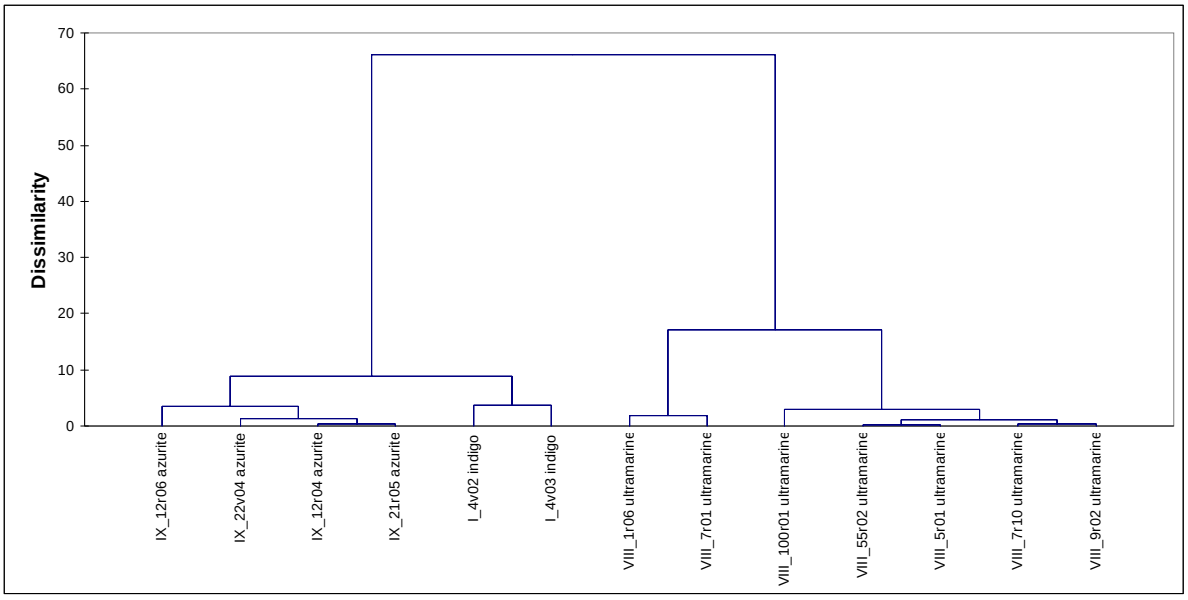

Figure 7- Cluster analysis on blue painted areas

A sort of protocol of analysis can therefore be proposed for miniature analysis, where several painted areas should be characterised:

1. FORS is firstly used to get a reflectance spectrum from all painted areas; where possible, pigments are identified according to their spectral features (i.e. reflectance maxima for blue and green pigments, inflexion points for yellow and red pigments);
2. Cluster analysis is then applied to spectra in ASCII format to identify painted areas obtained with similar pigments;

3. Raman spectroscopy is applied on the basis of the groups identified by cluster analysis, limiting its use to the analysis of one item for group;
4. XRF spectrometry is applied to characterise metal pigments, to verify superimposed painted layers and to identify contaminants in pigments

Using this protocol allowed shortening the overall time for application of the three analytical techniques, limiting in this way mechanical stress for the manuscripts otherwise obliged to stay open for long.

The palettes of the seven manuscripts are reported in Table 2. The only colour for which no response can be given is violet, present in manuscripts I, V and VIII. Due to the organic nature of violet painted areas (XRF yielded only light elements; Tyrian purple also must be excluded), it can be guessed, according to reflectance spectrum, the use of a dye such as kermes; another possible dye, cited by several medieval texts, could be turnsole, extracted from *Crozophora tinctoria* but its presence cannot be verified at present due to lack of a standard reference.

Manuscript	red	yellow	green	blue	gold
I	cinnabar, minium	-	-	indigo	copper/zinc/gold
IV	minium	orpiment	malachite	-	-
V	minium	orpiment	malachite	-	-
VI	minium	orpiment	malachite	-	-
VII	minium	orpiment	malachite	-	copper/zinc
VIII	minium	orpiment	malachite	ultramarine	copper/zinc
IX	minium	-	-	-	-
V (later unit)	cinnabar	-	-	-	-
VIII (later unit)	cinnabar, minium	lake	malachite	azurite	-
IX (later unit)	cinnabar	-	malachite	azurite	-

Table 2 - Palettes of the seven manuscripts from Bobbio analysed

The hypothesis of art historians of three stylistically different groups of manuscripts can be considered as confirmed by chemical analysis: palettes are consistent inside each group and slightly different among themselves. Other considerations can be drawn on the basis of the palettes. Manuscript I appears to be the most valuable due to use of cinnabar and gold (even if as an alloy with copper and zinc), as expected from the stylistical point of view. In manuscripts IV, V and VI a rather poor decorative style is reflected in the choice of less valuable pigments: green and yellow areas show little hiding power, as if they were painted as watercolours, i.e. highly diluted pigments; the lack of blue areas is also worth noting. With manuscripts VII and VIII a certain recovery of the *scriptorium* can be recorded both on the artistic side, with a much higher number of decorations, and in the choice of pigments, among which stand out a copper/zinc alloy to simulate gold foil and, mostly important, the highly valuable ultramarine blue in one of the first evidences ever recorded on European artworks. Finally manuscript IX, datable to the last period of production of the *scriptorium*, is again marked by a poor style and decorations obtained with red and black inks only.

One remarkable feature in the overall palette of these manuscripts is the use of a copper/zinc alloy in place of gold. Gold in the form of foil or powder (the so-called *shell gold*) is quite typical of miniature paintings, having been used since early Middle Ages to decorate illuminated manuscripts; in this case the use of a cheaper alternative can be seen as characteristic of a particular age, area or scriptorium being its occurrence rarely evidenced.

Final considerations concern evidences of later interventions or additions of different codicological units. Apart from being apparent from the stylistical point of view, these units are even simpler to detect on the basis of chemical analysis. We can consider as an example the two decorated initials shown in Figures 8 and 9. They apparently belong to different codicological units with respect to the main unit of the manuscript in which they are present. According to art historians, the initial on left, belonging to manuscript VIII, is a XII century production, while the initial on right, belonging to manuscript IX, is datable to the XV century. In both cases, as reported in Table 2, the palette used is clearly different from the main palette of the manuscript, confirming that different hands composed these initials.

Figure 8- Initial from manuscript VIII

Figure 9- Initial from manuscript IX

Conservation Problems

Analysis on the manuscripts revealed two important issues with concern to conservation problems. First of all, in several instances and on different manuscripts it was found evidence of degradation of minium to a blackish product. Raman analysis did not yielded any spectrum from the black areas, while UV-visible reflectance analysis yielded a spectrum similar to that of minium, i.e. a sigmoid with an inflexion point near 570 nm, but with a much lower reflectance in the red zone as expected for a black compound. Alteration can therefore tentatively assigned to oxidation of Pb_3O_4 to PbO_2, a phase known as plattnerite, whose occurrence in paintings has already been noted in some instances (Burgio *et al.*, 2001). The reason for this alteration is not known in the present instance.

Secondly, it was found evidence for a marked alteration on areas originally painted with a golden pigment that has turned to a green-brown hue. XRF spectrometry revealed the golden painted areas actually made of copper/zinc alloy (Figure 10), while Raman spectroscopy identified the presence of organic molecules that were charred upon laser irradiation; this made identification not possible under the present analytical conditions. Nevertheless, collection of a microscopic particle of this pigment from the gutters between sheets allowed execution of a Raman analysis in laboratory, which yielded a spectrum apparently due to a copper carboxylate of uncertain stoichiometry (Figure 11).

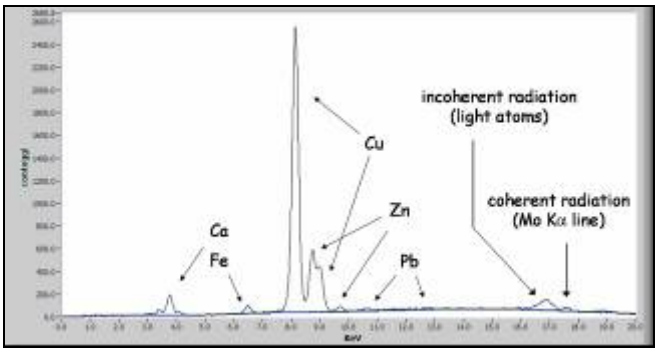

Figure 10- XRF spectrum of a golden painted area

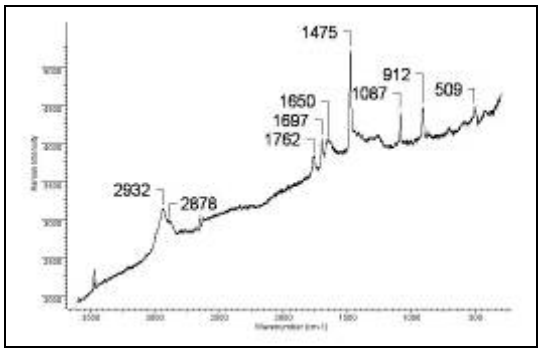

Figure 11- Raman spectrum of a golden particle

Alteration has therefore been attributed, in accordance with other researchers findings (Thickett and Odlyha, 1999; Trentelman *et al.*, 2002), to copper, used as a cheap substitute for gold, which eventually tarnished as a consequence of interaction with acetic acid and/or formic acid emissions from wood: this phenomenon was already noted on a IX century Italian manuscript held in the Archive and Chapter Library in Vercelli, Italy (Aceto *et al.*, 2008). These identifications make us think that copper/zinc alloy, as said before, was possibly a pigment typical of IX-X century miniature painting, at least among Italian illuminators.

CONCLUSION

To the authors' knowledge this is the first interdisciplinary study on manuscripts from Bobbio abbey, considered one of the most important scriptoria in Middle Ages in Italy. It concerns a limited set of manuscripts and should be completed at least with other three of similar dating, nevertheless it may be considered interesting in defining palettes in use in the late IX century-X century period by illuminators operating at the abbey. It is therefore desirable that this study could be implemented in the near future with analysis of more manuscripts held in different libraries.

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