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TECHNICAL PAPER

AN INVESTIGATION OF THE PALETTE AND TECHNIQUES OF SOME HIGH MEDIEVAL CODICES BY RAMAN MICROSCOPY

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A non-destructive investigation of inks and pigments used in late antiquity and in medieval codices has been undertaken. By comparing the results obtained on inkpots from Pompeii and from codices of various age, the use of metal gall inks appears to have been restricted to the period between the 1st and 4th centuries AD. A change in the use of pigments has been observed between the 9th and 12th century in the production of the Scriptorium of Nonantola (Italy). The increased wealth of the abbey could account for the use of expensive materials in the illuminations of the parchments.

1 Introduction

The reconstruction of the history of materials is a problem of vital importance to the study of objects of cultural heritage. The date of manufacture of an art work is difficult to establish, the literature being sometimes excessive and discordant, sometimes scant, and a precise indication cannot be given.[1] Much research has been carried out in recent decades on pigments and techniques used in the past. However, the terminus *ante quem* and *post quem* are frequently not clear. For example, there is some information on the presence of carbon based inks in the Roman periods and on the application of metal gall ink in the Middle Ages, but little information exists in the literature as to when iron gall ink was used for the first time.[2-4]

The guiding thread of this paper has been the identification of the ink present on the parchments of important codices. Commencing with an analyses of inks dating from late antiquity, the investigation accompanied the study of pigments and lakes, starting with some codices of the 6th century and extending to the great productions of the Benedictine monasteries in Northern Italy. In particular, the production of the Scriptorium of Nonantola was examined in this paper.

We have also tried to identify the chromatic rules known in subsequent times. It is important to examine a whole scriptorium to gain some idea of the evolution in taste, material, wealth and artists' pref-

erences. The association of materials for obtaining particular hues is also interesting since it can reveal the material association typical of a scriptorium and of an age. The type of codex is important in this respect; it matters greatly whether it is musical, liturgical, educational, historical, philosophical etc. The identification of the hands writing and illuminating the works or their parts could pose a very difficult but attractive problem for the future.

2 Experimental

A protocol was established for the execution of the research so that all the codices could be examined in the same way. An inspection of the codices with conservators was necessary in order to identify the pages to be studied before measurements were undertaken. Since there can be many codicological units in a codex, pages for analysis were chosen in all of them and, in each codicological unit, the selection included some pages from the beginning, the middle and the end in order to take into account material trends during execution. Care was taken to analyse the different hues in a painted area. The measurements were carried out in situ at the Bologna, Naples and Rome National Libraries by portable Jobin Yvon HE633, equipped with a 633 nm laser. A Labram of the Jobin Yvon-Horiba was used for ink samples, with a maximum power 5 mW. 50x and 100x long distance objectives were used to avoid contact with the parchments.

The spectra were visualised with the Grams AI program, which also enabled electronic research within the database.

53 codices pertaining to the ancient Benedictine Abbey of Nonantola, the Naples Dioskurides of the National Library in Naples and some inks found in Pompeiian atramentaria were considered.

3 Results and Discussion

Some of the spectra obtained from the parchments are reported below. The overall data are summarised in Table 1. First of all, a comparison was made in order to observe the changes that occur on passing from a fixed Raman instrument to a portable one (Figure 1). The spectra reported here show that identification is very simple in some cases, even with portable instrumentation, while in others it is difficult, especially when a high background hinders the recording of spectra, as was the case for the lakes. A loss of spectral resolution is evident, but the identification of compounds is possible by taking into account this fact and by preparing a database with the same instrumentation.

Among the examined inks, it was simple to identify iron gall ink or, more generally, metal gall ink from the bands recorded in 1500-1300 cm^{-1} range, as shown in Figure 1. In other cases, particularly until the instrument became stable, the signal was broader and the background higher than usual. Nevertheless, the peak at about 1450 cm^{-1} could be used for identification.

For carbon based inks the spectrum is simpler, with two bands at 1340 and 1580 cm^{-1}, at about

Pigment	before 1000 AD (29 manuscripts)	after 1000 AD (24 manuscripts)
Minium	90	67
Vermilion	20	83
Malachite	55	8
Vergaut	0	8
Indigo	10	67
Ultramarine blue	10	37
Orpiment	20	12
Yellow lake	27	37
Violet lake	6	8
White lead	6	8
Carbon black	3	0

Table 1: Frequency of use of pigments and dyes in Nonantola codices dated before and after 1000 AD.

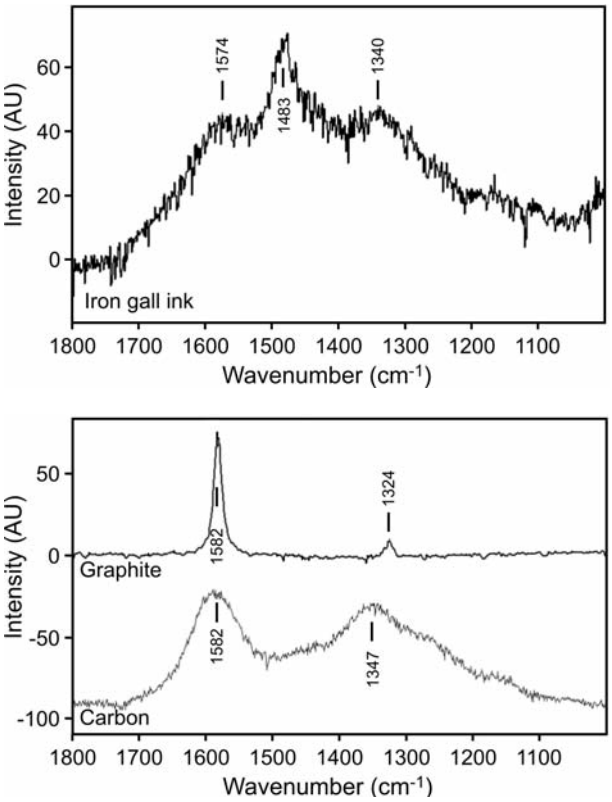

Figure 1: Raman spectra of iron gall ink, graphite and carbon.

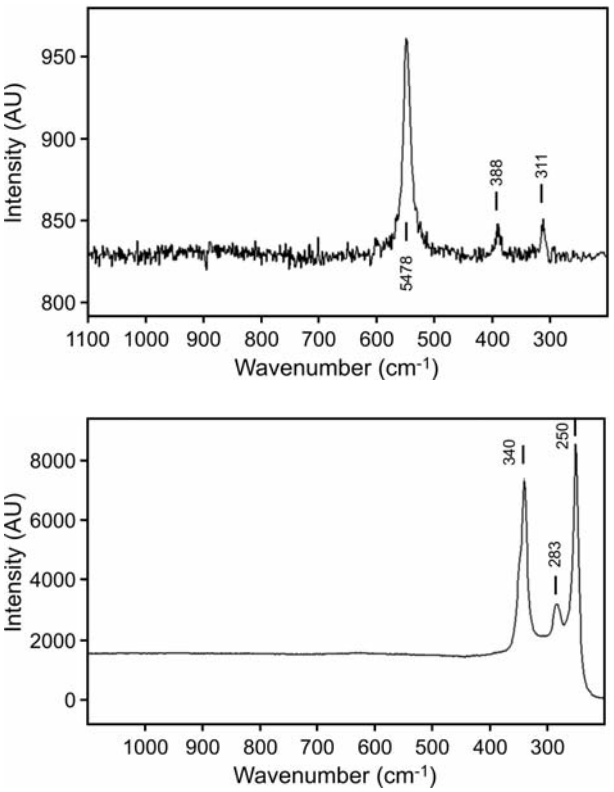

Figure 2: Raman spectra of a red spot of codex 1084, 10r (above, minium) and 4r (below, cinnabar).

the same wavenumbers as those of graphitic carbon, but of different shape and relative intensities, as can be seen in Figure 1.

According to an important historical source, Pliny the Elder, *atramentum sutorium* or Roman Vitriol (ferrous sulphate) reacts with tannin in skins forming a dark product. In effect, oak galls contain gallotannic acid that forms a black ink with vitriol. The practice of distempering a black material with gum arabic was known even in Ancient Egypt to yield a carbon based ink from about 2000 BC.

It was customary to write the titles or the incipit of a work with a red ink. This usage persisted in the Middle Ages, and it was verified also in our samples, e. g. in codex 1084, where the red letters were in minium or cinnabar (Figure 2).

The first sampling of inks was carried out on Pompeii (Figure 3a) and Herculaneum (Figure 3b) depositories, where many bronze or terra sigillata atramentaria can be seen, many of them preserved inside a residual ink. All the containers were shown to contain carbon based ink.

If the reaction between gall extract and iron was known, the problem which remains is to establish when metal gall ink was first used for writing. With the aim of finding this date, we examined some ancient and well dated manuscripts. One of the more ancient parchment codices was the Codex of

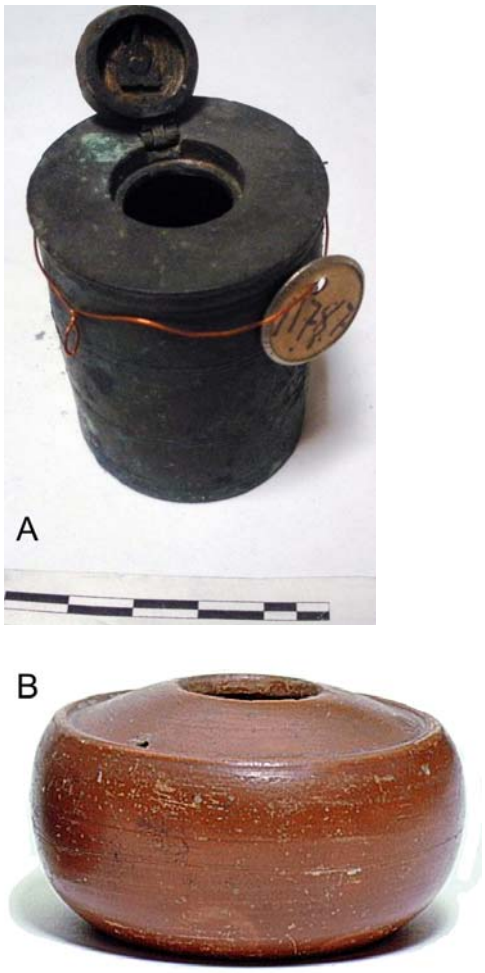

Figure 3: Ink containers in Pompeii (bronze, A) and Herculaneum (sigillata, B).

Ivrea dated to the 4th century, where the ink was assessed by Aceto et al.[5] by Raman microscopy to be of the iron gall kind.[5] Other important manuscripts still well preserved are the Dioskurides in Vienna (beginning of 4th century) and the Naples Dioskurides (end of 6th / beginning of 7th century). We had the opportunity to examine the Viennese Dioskurides, at least microscopically, in order to observe the scripts, the pigments and the pictorial technique used in its illumination for a comparison with their counterparts in the Naples Dioskurides. Raman measurements were carried out in situ on the Naples Dioskurides and the presence of iron gall ink assessed on the basis of the Raman spectra recorded. Therefore, it can be asserted that iron gall ink appears between the 2nd and the 4th centuries. Analysis of other important manuscripts falling inside this time period could restrict it further.

A comparison of the illuminations of these two important manuscripts shows that materials appear to be similar, though the Viennese Dioskurides is of a larger format and illuminated with greater precision. Investigations carried out

by x-ray fluorescence analysis revealed that lead red and cinnabar were applied in the codex.[6] It also appears that contours were traced in order to highlight the leaves' borders and nervatures and that, microscopically, there were mixtures of pigments in some areas.

In the Naples Dioskurides, where some pages are altered and there are losses to the pictorial surface in some small areas, the colours are still preserved, as can be argued by comparing the flower colours of the species indicated in the Greek text.[7]

The palette of the Naples Dioskurides identified by Raman microscopy comprises cinnabar (used in capitals), minium (in plants), hematite (in grounds), orpiment, indigo, azurite (not clear because of the weakness of spectra), carbon, a fluorescent violet lake, a yellow lake and lead white. The use of a mixture of indigo and orpiment for the depiction of all the green foliage is a relevant fact since this mixture has been identified in other old manuscripts and corresponds to the vergaut reported in the Jean Lebegue manuscript[2] and Theophilus.[3] Even without explicitly citing it, the recipe is also reported by Cennino[4] in chapter 53:

Del modo come si fa un verde d'orpimento e d'indaco (How to make a green with orpiment and indigo): Green is a colour made of two parts of orpiment and one part of indigo; they must be ground well together with clear water. This colour is good for painting.

Notable occurrences of vergaut are in Lindisfarne Gospels (about 715 AD).[8] In the Tours Gospel carbon, indigo, lead white, minium, orpiment and vermilion were identified, as in the Book of Kells.[9] These are, therefore, the more frequently used materials in the illumination of parchments in the more ancient manuscripts. This also appears to be the case for other important research done on illuminated manuscripts.[10-16]

The apparent absence of lead white in the Viennese manuscript may be a matter of preference, since it was used before and after in other contexts, or it may be due to the use of whiter parchments where illumination could be carried out with the technique "a risparmio" (using the support, without pigments). This fact could also be referred to the different places of execution: Constantinople rather than Ravenna.

After this period, many other items can be found in the libraries of old Benedictine Monasteries, such as those situated south of the river Po: Bobbio, Nonantola and Polirone.

We decided upon a closer and more extensive examination of the materials used in the scriptorium of Nonantola, a Benedictine abbey founded in 752 AD. In regard to the works executed in that scriptorium, also bought by the Abbey and used there, we made reference to the recent reconstruction carried out by Maria Pia Branchi[17] who, on the basis of old inventories and direct inspection, has traced 120 codices. In her book she stated that some codices were datable to and bought before the abbey's foundation, and from the 8th century onwards they were bought or written on the spot. Moreover, many codices were re-written after a fire had destroyed some important codices in the 12th and 13th centuries. We had permission to analyse 6 codices from Bologna University

Figure 4: The rubrication in the Naples Dioskurides (A); a leaf as painted in the Naples Dioskurides (B); a comparison between Aristolochia in the Naples Dioskurides (C) and a recent photograph of the plant (D).

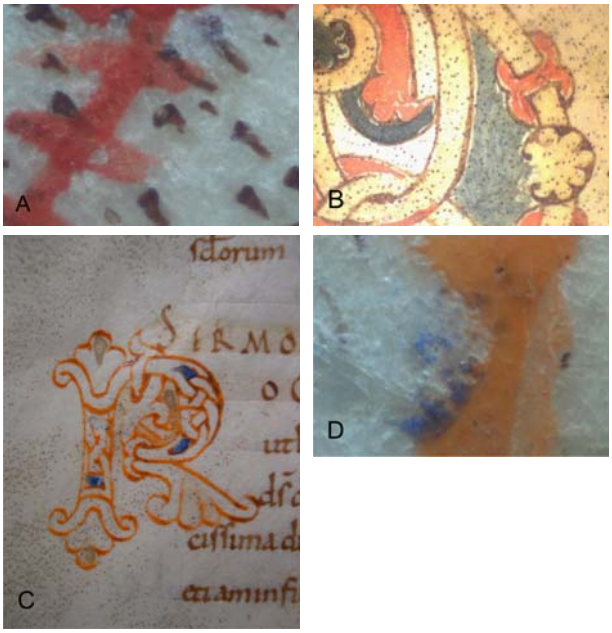

Figure 5: A detail of Rome Sessoriano 10 (A), of Sessoriano 33 (B); a polychrome letter of Bolognese "Sermones" with touches of colour (C) and a spot of Bolognese codex 2824 "Musicae Laudes" with ultramarine disease (D)

Library, 2 from the Capitular Library of Vercelli, 34 from the Sessoriana Collection and 11 from the Vittorio Emanuele Collection of the National Central Library in Rome, a total of 53 codices, which is a large proportion of extant works. The 11 codices of the Vittorio Emanuele Collection were recovered on the antiquarian market, in Italy and abroad and given to the Central Library.

Starting with the Bologna University Library, it must be pointed out that the codex 701, called Lactantius, contains only text and is one of those bought by the abbey. There are retouches to the inks with a blacker one – both were analysed with Raman microscopy to be metal gall ink.

The codex 1604 of the University Library of Bologna has some rubricated letters and some big letters at the beginning of paragraphs, such as the ones shown in Figures 4 and 5.

The codex 2248 “Sermones” is polychrome, with beautiful letters having touches of colour inside.

The manuscript 2824 “Musicae Laudes” is one of the surviving works with music in the style of Nonantola, the parchment is decorated and there is an example of the lapis lazuli illness due to acidity intervention (Figure 5D).

In the following deals with the codices preserved at The National Central Library in Rome. In these codices, a complexity is evident in the use of red pigments. Two compounds are under discussion: cinnabar and minium. In some areas there is only minium, in others only vermilion. It can be observed that the use of materials is specific to a given kind of letter: minium and vermillion are used for initials and rubricated letters respectively.

Sometimes minium and vermilion are used in admixture and this may be supposed to be due to the adulteration of vermilion. Alternatively, a trace of minium may be supposed to have been used in the past as a stabiliser of vermilion.[16]

In accordance with the execution phases of the artwork, a writer used a pen to write the two columns and an illuminator decorated the capital letters. The remaining question is who made the underlined letters? By comparing the data from codices before and after 1000 AD, it can be observed that:
- the use of minium decreases whereas that of vermilion increases, and this appears to be a preference, although the instability of minium at the time was known;
- for the green parts the only competing change is the use of vergaut after 1000 AD, whereas malachite was used before. The choice between ultramarine and indigo is not a real one, since the colours are different: blue for ultramarine, blue-green for indigo. They are both more frequently used after 1000 AD and this indicates an increase in polychromy and in the economics of using precious materials;
- with reference to yellows, it can be observed that a substitution of orpiment by a yellow lake is intervening but there are still some cases where the use of orpiment has been detected. The decline in the use of orpiment could be due to its toxicity, but the lake was not so beautiful and its use did not disappear later on. A violet lake is used in many instances, with occurrences accompanying that of white lead: both materials can be related to codices possibly not pertaining to the scriptorium of Nonantola.

4 Conclusions

From the analyses carried out it can be deduced that metal gall ink was used from the 4th to 12th centuries. As a rough estimation, we calculated the number of times the different materials were identified on the total number of codices and rounded off the results. The data in Table 1 was obtained in this way. There is an evolution with time in the use of pigments and dyes: some pigments, and generally the cheaper ones, had decreasing use, whereas others were increasingly used. An association of colours are observed that could be characteristic of a given scriptorium.

There is an increase in polychromy from the 8th to 12th centuries and this may be due to an increase in commercial contacts with other countries.

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