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Non-invasive in situ analytical techniques working in synergy: The application on graduals held in the Certosa di Pavia☆

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ABSTRACT

The old library of the Certosa di Pavia still holds thirteen graduals, choir-books with lyrics and scores. Their rich decorations were made by various artist–monks during the fiftieth century. In 2009, the gradual numbered 814 underwent a conservative restoration intervention under the supervision of the Certosa Museum Director, Letizia Lodi, to be on display in Verona, and later it was also included in the exhibition of Arcimboldo works in Milan (2011).

Non-invasive in situ analyses were performed on seven books of this collection, considering fourteen illuminated pages in total, painted by four authors: they showed different technical features, but the same typical materials. Pigments and binders were examined exploiting the synergy between four complementary techniques, namely, EDXRF (energy dispersive X-ray fluorescence), FORS (fibre optics reflectance spectroscopy), FTIR (Fourier transform infrared spectroscopy) and micro-Raman spectroscopy.

Summarizing the palette, the blue pigments used are ultramarine, azurite and, in one case, smalt blue; the red and pink hues are given by red ochre, vermillion and lakes; the yellow ones by orpiment, lead-tin yellow and yellow ochre. The white used is lead white, both in mixtures and as underpainting layer. The application of techniques with different penetration depths allowed to detect the stratigraphic sequences without sampling, opening to the interesting application to off-limits masterpieces. Intriguing is the case of green pigments, recognized as malachite and basic copper sulphates, but possibly also given as a mixture of copper-based and yellow pigments. The different kinds of gold and silver gildings were considered and investigated, accounting for different executing techniques for the different authors. The closing challenge will be determining the binders without any sampling, but exploiting FTIR spectra for the detection of organic binders.

1. Introduction

The work stems from a project that lasted two years and involved four different Italian universities, whose aim was a multidisciplinary approach to increase the value of Certosa di Pavia to make some of its hidden treasures available to visitors. Among the hidden parts, there is the old library that still holds thirteen choir-books, codices or graduals, forming an almost unrivalled collection, which are the object of this study.

Archive documents say that at the end of the eighteenth century, thirty-nine books were held in the Charterhouse Library, but after the suppression of the Carthusian order, they were lost and some of them were brought to France. After almost one century of peregrination, only thirteen of them were returned to Pavia: some of them had been divided, losing liturgical chronology and making it difficult to reconstruct the original sequence. We know that at least four different artist–monks worked on them, but owing to the fact that manuscript illuminators in general did not sign their work, the attribution of manuscript illustration can be difficult. Attributions made on the basis of style can be very reliable, but they may be strengthened and supported (or conversely, weakened and refuted) through scientific analyses. There are a lot of literature works [1–9] in which some analytical and micro-analytical techniques have been used to study painting materials applied in different manuscripts, but this is the first time that these four spectroscopic techniques (EDXRF, FORS, micro-Raman and FTIR) are

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together applied in situ obtaining a wide amount of data (Fig. 1). EDXRF (energy-dispersive X-ray fluorescence) is among the most cited analytical methods in the literature dealing with cultural heritage investigations. The major advantages of X-ray spectrometric measurements include spectral coverage for most elements present in the pigments ($Z > 16$), nondestructive and fast analysis and good precision and accuracy. The fact that analyses need to be performed in a non-destructive and, more importantly, non-invasive way is extremely important, as removing samples from the graduals is unacceptable. On the other hand, when analysing illuminated manuscripts, we are usually in a multiple-layer system and, using only EDXRF, it would not be possible to distinguish the information coming from the different layers. The combined use of FORS analysis (fibre optics reflectance spectroscopy) is surely useful to solve this inconvenient feature of EDXRF analysis. Concisely, diffuse FORS is based on selective absorption of materials due to molecular electronic transitions: the obtained reflectance spectrum exhibits characteristics—maxima, minima, shoulders—that are unique to different pigments. The identification of pigments in the most external layer by reflectance spectra allows us to inferthe composition of the underlying layers. The additional importance of FORS is related to the possibility of detecting with great accuracy pigments made with light elements, like ultramarine and lakes, which EDXRF cannot identify.

Micro-Raman spectroscopy is the technique of choice for illuminated manuscript analysis because it allows a rapid, unambiguous and in situ non-destructive approach for the examined objects. Since Raman spectroscopy probes molecular and crystal lattice vibrations, it is sensitive to the composition, bonding, chemical environment, phase and crystalline structure of the examined material and therefore it is able to unambiguously identify the majority of the pigments; furthermore, spatial resolution allows to discriminate among different chemical components in pigment mixtures and the measurements are free from interferences, except for the fluorescence due to the binding media and/or varnishes, that however were used in quite small quantities in painting [10].

Although the vibrational information obtainable by Raman spectroscopy is similar to that obtained by infrared spectroscopy (IR), it is not identical but rather complementary due to the different selection rules governing vibrational Raman scattering and IR absorption. When applied in the laboratory, Fourier-transform infrared (FTIR) spectroscopy offers a fast analysis of micro-samples and is able to provide information on the nature of the organic and inorganic materials used by an artist. Its application in the field in a non-invasive manner requires that measurements are performed in reflection mode and, even if several examples of such application are reported in the literature, it still deserves further exploitation [11–15].

One of the books was restored in 2009 by the Laboratory of Benedictine Nuns, which was qualified for old manuscripts. On this occasion, a complete digitization was done by taking advantage of the availability of single sheets. Scientific analysis and material characterization were not done during restoration and this opportunity also allows a verification of the possible effects of the conservative work.

Only a few scholars could access the complex of codices held in Certosa di Pavia, so this work focused on acquiring as much shareable data as possible. The performed joint use of these four non-invasive analytical techniques better characterizes the materials (pigments, glazes, ligands, finishes, metallic foils…) and the techniques (mixture of pigments, pigments overlaps, gilding techniques…) of these books.

2. Materials and methods

Due to the fragility and preciousness of the codex considered in this work, all the analyses had to be performed in situ in the room where they are usually held, thus exploiting only portable instruments. The ultimate goal was to try to reconstruct the pictorial techniques, besides the materials used: this information will be of great help for the attribution of the single miniatures, joining the archive research and the stylistic considerations.

2.1. Sample description

The thirteen books now held in Certosa are made with parchment pages (90 × 62 cm); each book has 70 pages on average, except for

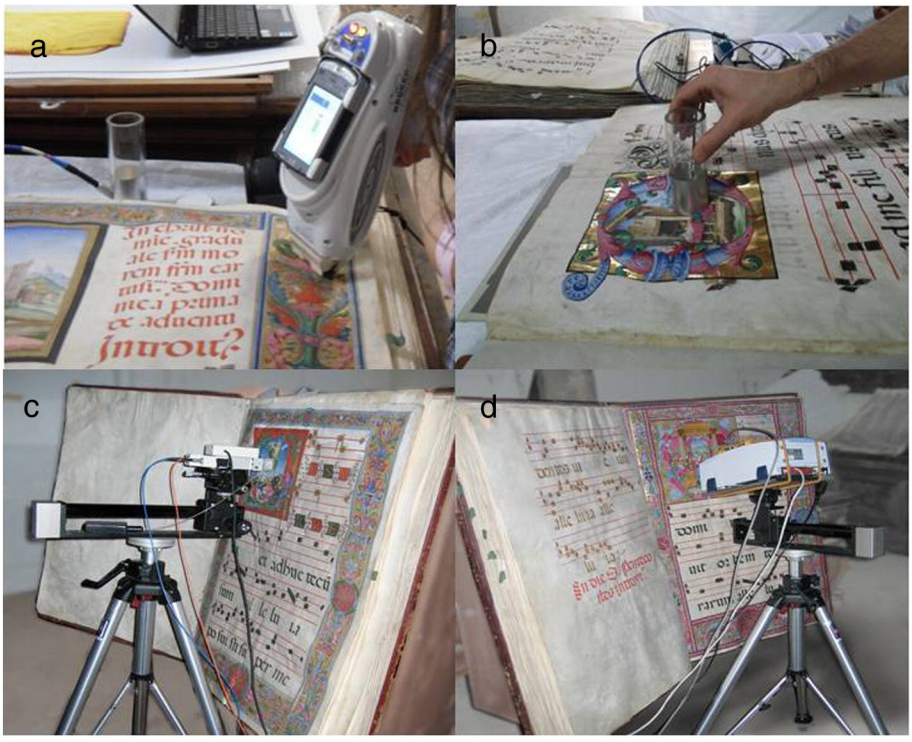

Fig. 1. The instruments at work in situ. (a) EDXRF instrument (Tracer III SD, Bruker); (b) Vis-NIR spectrophotometer (HR4000, Ocean Optics); (c) FTIR spectrophotometer (Alpha, Bruker); (d) Raman micro-probe (Jasco RMP-100 probe interfaced to a Lot-Oriel MS125 spectrometer).