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Hyperspectral Imaging and Raman Analyses of the Red Decoration of the St. Mauro Altar in St. Salvatore's Church (Pavia).

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***Abstract* – In the basilica of St. Salvatore, antependiums belonging to different phases of monument decoration are visible. The most valuable, the marble frontal of the high altar, dates to 1511 and is probably the only one from the first decorative phase of the church. The side altar frontals appear to be made of wood, embroidered damask, or other fabrics. They are partly related to the renovations the basilica underwent when it was reopened for worship in the early 20th century, except for this frontal in St. Mauro's Chapel, which was plausibly made during the early 18th-century redecoration of the chapel itself.**

Because of its style and construction, it is assumed to belong to the Baroque decorative phase, referring to the date "1709" painted on the vault. This hypothesis is being verified by means of art-history research supported by the diagnostic study of the materials. The analyses, which are ongoing, were initially conducted on the red areas of the artefact, using portable Raman and visible reflectance spectroscopic techniques. Subsequently, measurements were taken with a hyperspectral camera, obtaining images highlighting the spatial distribution of the red pigments on the frontal.

I. INTRODUCTION

The frontal of St. Mauro's altar has a compositional typology that recalls a generally widespread pattern in the altars' frontals of the 17th-18th century, whether they are made of wood, marble, embroidered fabric, leather, or embossed silver. It presents a design characterised by plant motifs, incorporating in the centre and on the sides a sort of clypeus or medallion in fake marble with white veins surrounded by a dense tangle of decorative plant motifs and birds. The ornamental system is symmetrical: the two parrots look towards the centre, while on the sides, two large pairs of volutes contrast with the central motif and two large racemes branch off from below, spreading apart in other volutes and sometimes meeting with the spinners. The background is white, and this brings out with greater emphasis the colour of the volutes and the coloured vegetable spirals (Fig.1).

The scagliola technique had spread to the Po valley by the end of the sixteenth century, especially in the Emilia area [1]. There had not been precise bibliographical references on the use of this technique until the last decades of the sixteenth century. The first Italian testimony is a plan signed by the Mirandolese Pietro Baseghini dated 1629. In Lombardy, the production of scagliola dates back to the 60s of the seventeenth century, and the leading shops were found in the Intelvi Valley. Following the Council of Trento in 1545, there was a progressive increase in the use of sumptuous colours to decorate altars. This frontal is attributed to the period at the turn of the year 1709. Indeed, that date is painted on the fresco decoration of St. Mauro Chapel's vault, whence its likely attribution to the 18th century and not to the first decorative phase of the church, dating to the beginning of the 16th century.

On the occasion of recent restoration work on the frontal, it was possible to carry out a series of non-invasive spectroscopic measurements, performed both with the more traditional techniques, that is, by means of Raman – which is especially useful in identification of mixture of pigments and dark and black pigments –

Fig. 1. Overall view of the frontal; the red squares indicate the points where cinnabar was identified, whereas the red circle indicates the restored point where red ochre was found.

portable FTIR and visible reflectance spectroscopies [2-12], and with an innovative hyperspectral camera.

Hyperspectral imaging is a novel analytical technique based on spectroscopy, with the aim of measuring the spectrum of the light coming from each point of a scene of interest. While the human eye has receptors only for three colours, blue, green and red (RGB), hyperspectral imaging measures the continuous spectrum as a function of the wavelength λ of the light for each pixel (x,y) of the scene with fine spectral resolution. The collected data form the so-called hyperspectral image: a 3-dimensional data-cube as a function of x, y and λ. This data contains an extensive amount of information, and many numerical methods and algorithms have been developed to enable the extraction of quantitative parameters related to the physicochemical properties of the imaged objects, as well as the clustering into different components. One of the major fields of application of this technique is conservation science and the work of art analysis, where hyperspectral imaging represents a powerful diagnostic and non-invasive tool for studying artwork, characterising various materials such as stone, pigments and textiles, and revealing stability issues in paintings and sculptures.

During the first measurement campaign on the frontal, it was decided to focus on the study of red pigments. In this study it is shown how the combination of Raman and reflectance spectroscopies with hyperspectral imaging has allowed on the one hand to uniquely characterise the different red pigments used for the decoration and on the other to obtain overall images of the frontal that make it possible to visualise the areas where these colours were used.

It is worth noting that the red pigments generally used for the decoration of scagliola are those that are more stable in contact with plaster [13]. Generally, therefore, these are natural and burnt earths based on iron oxide and bright reds of vegetable origin such as madder and purple lacquer [14]. In this case, in addition to red ochre, a widespread use of cinnabar was revealed, which is a much more expensive and rarer pigment than those previously listed, indicating a rather important commissioner [15].

II. MATERIALS AND METHODS

A. The frontal

As mentioned previously, the frontal was made with the scagliola technique. It is one of the many art-forms created from ancient times still in use today to decorate surfaces to imitate marble. Scagliola is technically a putty based on pulverised selenite - crystalline gypsum (secondary gypsum) - which is very common in nature and which, under specific pressure conditions, deposits itself in layers. Its formation is made up of scales, flakes and splinters that have the characteristic of being translucent, able to let light pass partially through. Because of this characteristic, selenite was widely used in ancient Greece to make slabs to be placed at the openings of walls to protect the interior but allow in a light similar to that of moonlight (Selene in Greek). Also, Pliny, in his "Naturalis Historia", gives a long discussion of that material.

In the preliminary stages of the intervention, the cover of the frontal was observed with a polarised digital microscope. The cover is the slab that was smoothed with water, sponge, pumice, or other abrasive stones. Subsequently, it could be polished with linseed oil or walnut oil and then be marked by the transposition by sprinkling or tracing the design of the decoration. The observation under a polarised digital microscope highlighted the traces of a preparatory drawing, then apparently engraved with gouges of various shapes, hammer and chisel, to carve the parts that would have received the drawing brought back to dust on the plate, filled with liquid scagliola, coloured with vegetable and mineral pigments. These digging, filling and smoothing operations repeat themselves depending on the complexity of the design. Finally, the intervention with sanding and polishing protects the product from moisture, ensures resistance and waterproofing properties and highlights the colours with a possible final surface treatment with beeswax.

B. Spectroscopic techniques

The hyperspectral images were measured with a HERA VIS-NIR hyperspectral camera from NIREOS SRL (Fig.2). The camera, based on a novel Fourier-Transform approach, guarantees high-quality data even at low illumination intensities, which is typically recommended in the cultural heritage field in order not to

Fig. 2. "HERA VIS-NIR" hyperspectral camera from NIREOS SRL

damage the works of art. The camera features a high spatial (1280x1024 pixels) and spectral resolution (1.5 nm at 400 nm wavelength), a broad spectral coverage (400 – 1000 nm) and an easy point-and-shoot approach, without requiring any moving parts.

For these measurements, the sample was illuminated with a custom light source, comprising white LEDs and halogen lamps, and providing light in the 450 – 1000 nm spectral range. The overall measurement time was approximately 30 seconds. The calibrated reflectance data was obtained by normalizing the hyperspectral data with a white panel and a white 1-inch reflectance standard (Spectralon® Diffuse Reflectance Standards from Labsphere Inc).

Raman analyses were carried out by a portable BWTek i-Raman EX instrument provided with an Nd-YAG laser emitting at 1064 nm; the measurements were executed by means of a fibre optic probe directly on the altar. The spectra were taken in the spectral range 200-2500 cm-1 and were acquired by means of the BWSpec software with an average of 20-40 scans. The pigments were identified by comparing their spectra to the ones present in the literature.

Visible reflectance analyses were obtained with a Konica Minolta CM 2300d portable spectrophotometer, taking the measurements directly on the different coloured areas of the altar. The instrument calibration was made through a white 100%-reflective reference and a 0%-reflective calibration box. Visible reflectance spectra were recorded in the 400-700 nm wavelength range.

III. RESULTS AND DISCUSSION

Raman measurements allowed recognition of cinnabar (HgS) on some of the red decorative plant motifs and on the birds' wings (red squares in figure 1) by the bands at 253, 284 (sh) and 343 cm^{-1} [16]. Conversely, on the red area surrounding the restored part on the left side of the altar, the resultant decoration was made of red ochre (red circle in figure 1), characterised by the bands at 290 and 409 cm^{-1} [17]. All Raman spectra also showed the peculiar bands of gypsum at 1009 and 1135 cm^{-1} [18]. Visible reflectance measurements performed on the same area, confirmed those results. Indeed, visible reflectance spectra of cinnabar and red ochre, albeit not as straightforwardly different as Raman ones, are readily distinguishable.

Then, the hyperspectral image of the altar was taken. Fig.3 shows the results obtained for cinnabar with the HERA hyperspectral camera. In particular, Fig. 3A shows the RGB reconstruction of the altar, whereas Fig. 3B reports in red false colour the spatial distribution of cinnabar employed by the artist. This map has been obtained by applying a spectral angle mapper algorithm, which automatically identifies all the pixels that are spectrally similar with respect to a reference one (highlighted in yellow in the figure).

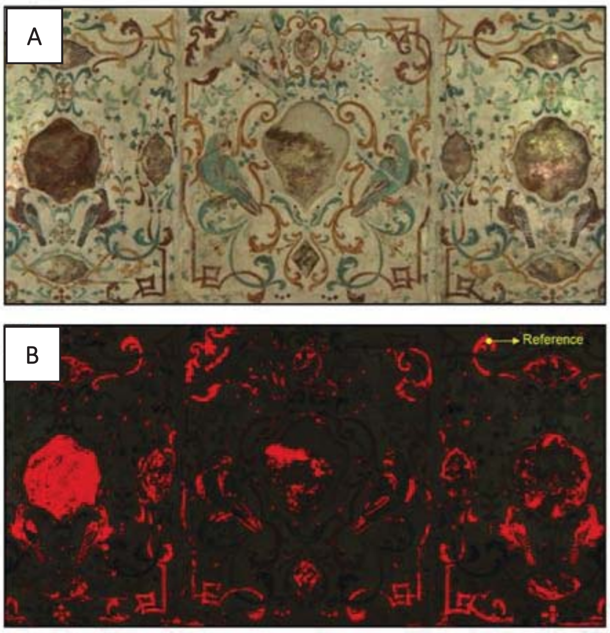

Fig. 3. In 3A, RGB reconstruction of the altar, in 3B spatial distribution of cinnabar (red false colour).

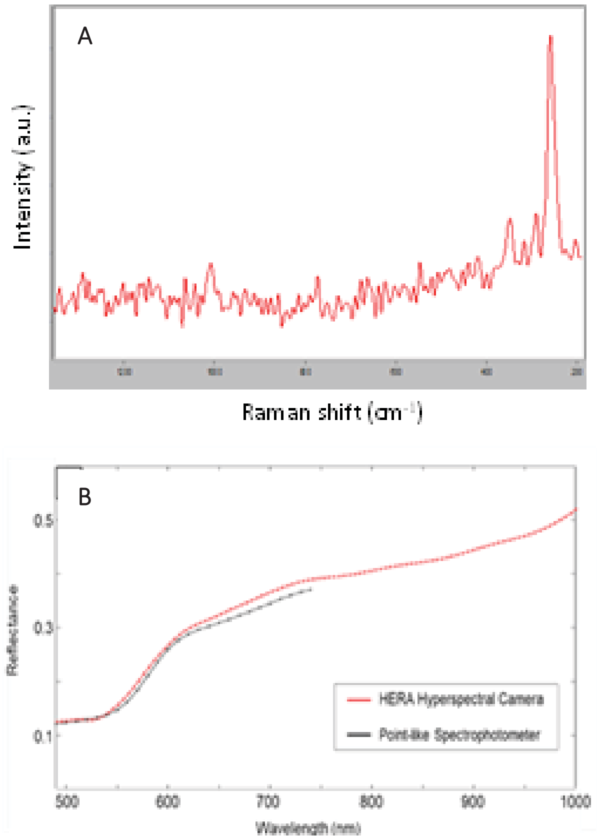

Fig. 4. A) Raman spectrum of cinnabar obtained on one of the frontal's red details; B) reflectance spectra of obtained on the same point with the point-like spectrophotometer (blue dotted line) and the HERA camera (red line).

As a reference point, one of the areas where cinnabar had been previously identified by Raman was chosen (Fig. 4A).

The reflectance spectrum of the reference pixel in Fig. 4B, was measured both with the HERA hyperspectral camera and the point-like spectrophotometer. The two spectra are in good agreement and confirm that the employed pigment is cinnabar.

IV. CONCLUSIONS

In this work single-point Raman and visible reflectance spectroscopies and hyperspectral imaging techniques were used synergically to both identify and map the red pigments utilised for decorating the beautiful frontal of St. Mauro Chapel's altar.

It is worth mentioning that all the measurements were taken in situ and without any sampling, proving the potentiality of spectroscopic portable devices in the identification of materials of artistic interest.

Moreover, it is important to underline the importance of having available single-point and imaging spectroscopic techniques. In fact, this multi-technique approach not only allowed identifying the different red pigments on some of the measured areas, i.e. cinnabar and red ochre, but also permitted obtaining the detailed whole distribution of the selected pigment in a relatively short time.

Finally, it is also to stress the use of precious cinnabar for decoration, denoting its importance as well as the wealth of its commissioner.

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