

# Spectroscopic Investigation of a 17th-Century Illuminated Parchment from *S. Maria di Montalto Church (Messina, Italy)*

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**Abstract** – In this paper, a combined approach involving X-ray Fluorescence (XRF) spectroscopy, micro-Raman spectroscopy and Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance geometry (FTIR-ATR), was employed to characterize, both at elemental and molecular scales, the raw materials and pigmenting agents used for the realization/decoration of a 17th-century illuminated parchment belonging to the *S. Maria di Montalto Church (Messina, Italy)*. In particular, the analysis of both blank and decorated areas allowed for the identification of original materials and later additions, as well as degradation patterns affecting the parchment surface. Notably, the obtained results represent a fundamental step toward the development of targeted, minimally invasive conservation strategies, aimed at ensuring the long-term preservation of this important historical object.

## I. INTRODUCTION

Parchments, also known as *charta pergamena*, have played a significant role in human history since the Middle Ages as writing support for recording historical texts, manuscripts, and books [1,2]. Produced from animal skins, such as those of sheep, calves and goats, their realization varies according to the specific geographical region and evolved following precise historical trends. One of the most precious varieties involved the employment of skin taken from the *foetuses* of lambs, named *charta virginea*,

which resulted in white scrolls characterized by high mechanical features and low thickness. The term “illuminated”, originally describing the use of gold—occasionally silver—to embellish the text, refers to a handwritten document with decorative elements, including ornate initials, elaborate borders, and miniature illustrations. The production of illuminated parchments required a complex, collaborative process that brought together scribes, illuminators, and binders. These decorative elements were not merely ornamental; they served to convey theological, political, or cultural meaning, and could guide the reader’s interpretation of the text.

In this scenario, the scientific investigation of illuminated parchments provides critical insights into their material composition, production techniques, and long-term preservation needs [3-5]. Knowledge of such aspects enables the reconstruction of both ancient and early modern artistic practices, regional production trends, and conservation standpoints for the development of tailored, evidence-based strategies to stabilize and preserve such mild materials. Moreover, the identification of biological degradation patterns informs appropriate environmental

controls and handling protocols. Noteworthy, the material characterization also contributes to authentication studies, and can assist in dating undated manuscripts through comparative pigment analysis [6,7].

In this context, this work reports some preliminary results obtained for a written illuminated parchment dating back to the 17th-century, belonging to the archive material of the *S. Maria di Montalto* Church in Messina (Italy), through a combined approach involving X-ray Fluorescence (XRF) spectroscopy, micro-Raman spectroscopy and Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance geometry (FTIR-ATR). The elemental and molecular composition of both blank and decorated areas allowed the possibility to shed light into the artist's manufacturing technique, typical of a specific production "school", and to locate, temporally and geographically, the artwork itself. Furthermore, the identification of possible degradation patterns extending on the surface not only provided information on the current state of conservation but also furnished a remarkable contribution to the choice of the best consolidating products in view of future restoration strategies to be applied.

It is worth of note that the obtained results fall within the framework of the "protocol agreement" for cooperation activities aimed at the restoration of archive materials belonging to the *S. Maria di Montalto* Church (Messina, Italy), among the Superintendence BB.CC.AA of the Sicilian Department of Cultural Heritage and Sicilian Identity, the Department of Mathematical and Computer Sciences, Physical Sciences and Earth Sciences of the University of Messina and the Regional Centre for Planning and Restoration and for Natural and Applied Sciences for Cultural Heritage of the Regional Department of Cultural Heritage and Sicilian Identity<sup>7</sup>.

## II. MATERIALS AND METHODS

### A. The parchment

The investigated parchment, known as "*D.O.M. Sancto Ignatio Loyola Societatis Iesu Fundatori...*", consists of a single sheet of  $\sim 531 \times 293$  mm decorated only on the *recto* side, belonging to the archive material of the *S. Maria di Montalto* Church (Messina, Italy). In particular, the parchment is a devotional and commemorative document dedicated to *Saint Ignatius of Loyola*, founder of the Society of Jesus. Starting from the top, a painted medallion depicting the saint, richly dressed and holding an open book, likely symbolizing the spiritual rule of the Jesuit order, can be observed. The surrounding frame is decorated with gold motifs, bordered by deep red/violet tones. At the center, a "golden" text commemorates a noble act of piety by a woman named *Josepha Maria Caloria*, who, in 1653, offered some deed in devotion, possibly linked to her religious vocation. Surrounding the text, ornamental calligraphic monograms can be seen,



Fig. 1. Recto of the "*D.O.M. Sancto Ignatio Loyola Societatis Iesu Fundatori...*" parchment after restoration, with the position of the analysed points indicated.

while at the bottom lies a heraldic crest rendered in vibrant hues surrounded by classical baroque scrollwork.

In this study, we selected 10 points of the *recto* (labelled as D#, with # = 1, ..., 10) and a single point of the *verso* (not decorated, D11, not shown), for XRF,  $\mu$ -Raman and FTIR-ATR analyses.

### B. Methods

XRF measurements have been collected through a portable XRF "Alpha 4000" (Innov-X systems, Inc., Woburn, MA, USA) apparatus, capable to detect chemical elements with an atomic number (Z) ranging from 15 (phosphorus) to 82 (lead). The instrument is equipped with a Ta anode X-ray tube as the source and a Si PIN diode (active area of  $170 \text{ mm}^2$ ) as the detector. For each point, two consecutive tests were performed through the following operative conditions: 40 kV and  $7 \mu\text{A}$ , and 15 kV and  $5 \mu\text{A}$ , for the first and second run respectively, over a total spectrum collection time of 120 s. The instrument has been controlled by a Hewlett-Packard iPAQ Pocket PC, also used for the data storage. The calibration has been performed using a soil light element analysis program (LEAP) II and verified using alloy certified reference materials produced by Analytical Reference Materials International.

Micro-Raman measurements have been collected using a portable Raman "BTR 111 Mini-Ram TM" (B&W Tek,

Inc., Newark, NJ, USA) spectrometer. The instrument is provided with a 785 nm diode laser source and a thermoelectrically cooled CCD detector, with a 280 mW maximum laser power at the excitation port. Spectra were registered in the 62–3150  $\text{cm}^{-1}$  wavenumber range with a resolution of 10  $\text{cm}^{-1}$  and an acquisition time of 10 s  $\times$  16 scans. The system was supplied of a BAC151B Raman microscope mounting an 80 $\times$  objective which guaranteed laser beam spot size of 25  $\mu\text{m}$  on the surface with a working distance of 1.25 mm. The laser maximum power delivered to the samples was  $\sim$  15 mW. Band assignment was carried out by comparing the experimental spectra with data reported in various databases and the literature [8-10].

FTIR-ATR Data were recorded in the 400–4000  $\text{cm}^{-1}$  wavenumber range using a DA8 Fourier transform infrared (FTIR) spectrometer (BOMEM, Canada), operating with a Globar source, in combination with a KBr beamsplitter and a thermoelectrically cooled deuterated triglycine sulphate (DTGS) detector. Investigated samples were placed in contact with the surface of the ATR crystal contained in the Golden Gate diamond ATR system, based on the Attenuated Total Reflectance (ATR) technique. A resolution of 4  $\text{cm}^{-1}$  was used, by adding 100 repetitive scans, in order to guarantee a good signal-to-noise ratio and highly reproducible spectra.

### III. RESULTS AND DISCUSSIONS

Figure 2 reports, as example, the XRF, micro-Raman and FTIR-ATR spectra collected on points D3 and D8, respectively associated to a golden area within the medallion at the bottom, and a letter of the text, as representative of golden areas of the *recto* of the parchment. The XRF spectrum collected on point D3 almost completely matched that of D8, suggesting a comparable elemental composition. In particular, high concentrations of Au were observed from the high intensity peaks at  $\sim$ 9.71 keV and  $\sim$ 11.44 keV, alongside with calcium (Ca), likely related to the calcination process, and lead (Pb) from the preparatory layer. Interestingly, the significant concentration of gold suggests the application of a gold leaf or direct gold powder for the realization of gilded decorations, as well as “ink” for the text, highlighting a remarkable commitment of the artist.

Concerning the molecular characterization, micro-Raman spectra (Fig. 2b) showed the presence of organic components, presumably ascribable to an organic-based binding medium, together with a characteristic low frequency metallic feature. Finally, the FTIR-ATR spectra (Fig. 2c) allowed us to distinguish the presence of calcite, collagen, and cellulose, the latter deriving from application of methylcellulose ( $\text{C}_{20}\text{H}_{38}\text{O}_{11}$ ) during restoration interventions.

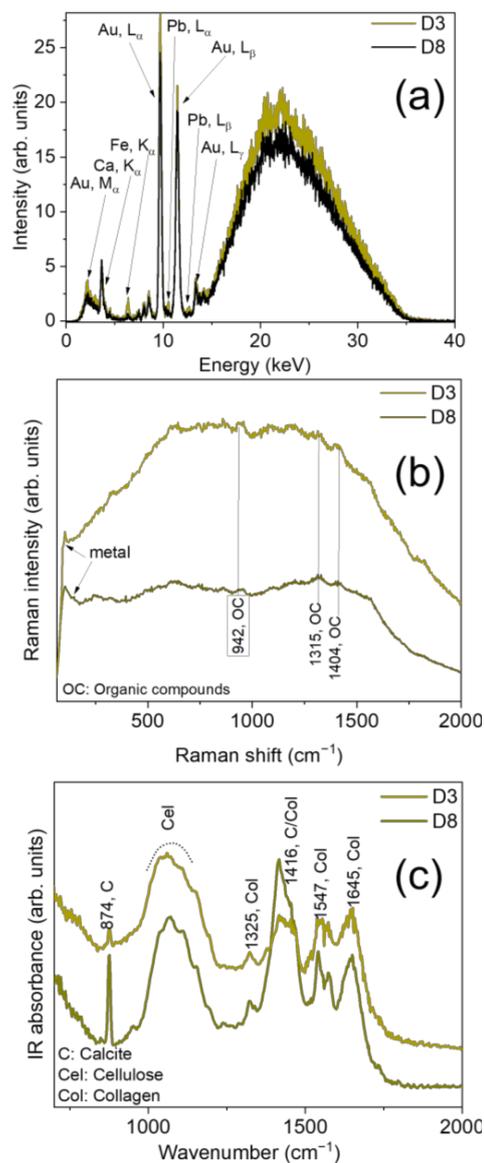


Fig. 2. (a) XRF, (b) micro-Raman and (c) FTIR-ATR spectra collected on points D3 and D8 of the parchment.

Concerning the red-colored areas of the parchment, Figure 3 shows the XRF (Fig. 3a) and micro-Raman (Fig. 3b) spectra collected on two points, *i.e.* points D1 and D10, associated to a red decoration of the heraldic crest at the bottom, and to the red/violet motif of the frame around the text (see Fig. 1). First of all, two different red pigments were recognized for the realization of the red/reddish decorations. More in details, concerning point D1 (as reasonably in all areas highlighted in light blue in Fig. 3c), the elemental analysis revealed, as main result, the presence of mercury (Hg), from the observation of its characteristic lines centered at  $\sim$ 9.98 keV ( $L_{\alpha}$

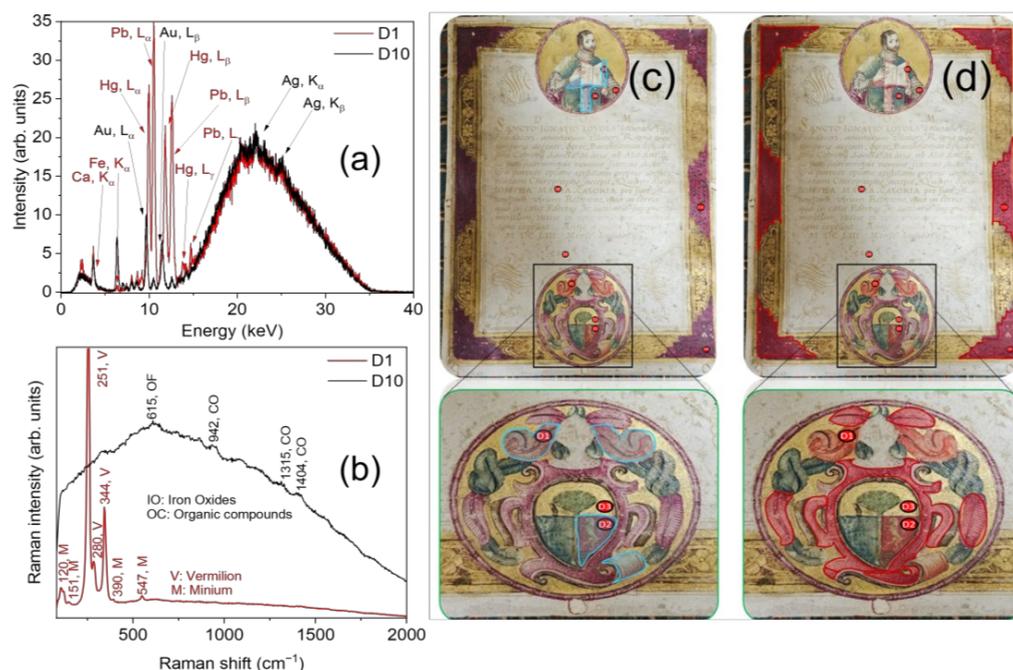


Fig. 3. Comparison of the (a) XRF and (b) micro-Raman spectra collected on point D1 and D10, representative of the red decorations within the medallion at the bottom and of the deep-red/violet motifs surrounding the text on the recto of the “D.O.M. Sancto Ignatio Loyola Societatis Iesu Fundatori...” parchment. Panels (c) and (d) show the distribution of the corresponding identified pigments on the parchment surface. See text for details.

transition),  $\sim 11.82$  keV ( $L_{\beta}$  transition) and  $\sim 13.83$  keV ( $L_{\gamma}$  transition), suggesting the use of vermillion ( $HgS$ ) for the red/brown decorations. Moreover, Pb, Ca and Fe were also distinguished. Going on, micro-Raman analysis allowed us to confirm the presence of vermillion ( $HgS$ ) through the observation, in agreement with previous literature [11], of the low-frequency contributions centered at  $\sim 252$   $cm^{-1}$  ( $A_{1g}$ ),  $\sim 288$   $cm^{-1}$  ( $E_g$ ) and  $\sim 347$   $cm^{-1}$  ( $E_g$ ), supporting our previous XRF results. Interestingly, such compound turned out to be in mixture with few amounts of minium ( $Pb_3O_4$ ), identified through the observation of spectral features centered at  $\sim 120$   $cm^{-1}$ ,  $\sim 151$   $cm^{-1}$ ,  $\sim 390$   $cm^{-1}$  and  $\sim 547$   $cm^{-1}$  in the corresponding micro-Raman spectrum (red line in Fig. 3b).

As far as the point D10 is concerned, a completely different composition, both at elemental and molecular scale, was retrieved, suggesting that this color was applied at a later stage, or as a result of non-documented restoration interventions (see red highlighted areas in Fig. 3d). In particular, only Au and silver (Ag) were detected through XRF, whilst few amount of iron oxides and organic compounds were distinguished by micro-Raman spectroscopy.

Figure 4 reports, as example, only the FTIR-ATR spectra collected on points D9 and D11, respectively representative of undecorated areas of the *recto* and *verso* of the parchment. Concerning the *recto* side (point D9), FTIR-ATR analysis allowed us to unambiguously recognize the employment of collagen, a fibrous protein of the animal connective tissue, indicating an animal-skin support, together with calcite (residue from the

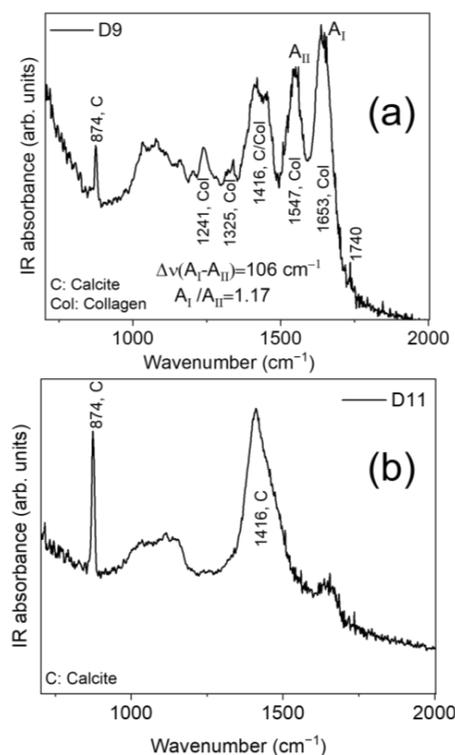


Fig. 4. FTIR-ATR spectra collected on point (a) D9 and (b) D11, representative of undecorated areas on the *recto* and *verso* of the parchment “D.O.M. Sancto Ignatio Loyola Societatis Iesu Fundatori...”.

calcination process). More in detail, the degradation state of the collagen-based fibrous matrix was assessed by evaluating the FTIR-ATR intensity ratio between the primary ( $A_I$ ) and secondary ( $A_{II}$ ) amide bands ( $A_I/A_{II}$ ), as well as the gap between their respective frequency-centres (see Figure 4a), being these parameters particularly sensitive to alterations caused by hydrolysis or gelatinization processes. Notably, the  $A_I/A_{II}$  ratio was found to be equal to 1.17, suggesting a not-negligible alteration of the fibrous network. Moreover, the observation a spectral features at  $\sim 1740\text{ cm}^{-1}$  supports the existence of oxidative degradation.

Concerning the *verso* side, only the absorption contributions related to the presence of calcite can be distinguished.

#### IV. CONCLUSIONS

In this work a non-invasive, multi-analytical investigation was carried out on a 17th-century illuminated parchment known as “*D.O.M. Sancto Ignatio Loyola Societatis Iesu Fundatori...*”, belonging to the archive material of the Church of *S. Maria di Montalto* in Messina, Italy. A combined approach involving X-ray fluorescence (XRF) spectrometry, micro-Raman spectroscopy, and Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance geometry (FTIR-ATR) enabled a comprehensive characterization of the parchment's composition both at elemental and molecular levels, revealing the use of materials typical of the historical period and underscoring, at the same time, the manuscript's high artistic and historical value. It is worth of note that these findings not only contribute to the broader appreciation of this cultural artifact but also establish a valuable, non-invasive strategy aimed at planning future conservation and preservation efforts.

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