2025 IMEKO TC26 International Conference on
Metrology for Archaeology and Cultural Heritage
Bergamo, Italy, October 15-17, 2025

Multi-technique archaeometric investigation of a XVII century illuminated parchment belonging to the *S. Maria di Montalto* Church (Messina, Italy)

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***Abstract* – This work reports some preliminary results of a non-invasive multi-technique approach involving X-ray Fluorescence (XRF) spectroscopy, micro-Raman spectroscopy and Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance Geometry (FTIR-ATR), for the characterization of a XVII century illuminated parchment belonging to the *S. Maria di Montalto* Church (Messina, Italy). In particular, starting from the assessment of the elemental and molecular composition of both blank and decorated areas, the nature of the raw materials and pigmenting agents used for the realization/decoration of the artefact was retrieved, allowing the possibility to discriminate between original and modern constituents, as well as to identify any possible degradation pattern. It is worth of note that obtained results provided a solid groundwork for the development of targeted and minimally invasive conservation strategies, aimed at ensuring the long-term safeguarding of this significant historical artifact.**

I. INTRODUCTION

Illuminated parchments are membranaceous writing supports crafted from various animal skins, including those of sheep, goats, and calves, and decorated with miniatures, *i.e.* hand-made illustrations realized through bright colors, gold and silver. They represent the primary writing medium of the majority of documents of cultural relevance, particularly in the Middle Ages and the Renaissance period, such as liturgical books, bibles, scientific texts and literary works. The manufacturing process typically involves steps such as washing and salt-curing, depilation, stretching, drying, scraping and pouncing. The resulting parchment assembly is strongly influenced by the geographical area and historical period of its production, making each piece unique in terms of quality, texture, thickness, and color. In the past few decades, the scientific investigation of parchment artifacts through the employment of complementary non-invasive (or, at least, micro-destructive) methodologies, represented a well-established approach for retrieving information about the historical-artistic context, manufacturing technology and long-term preservation of such assets [1-3]. In this context, the physico-chemical characterization of raw materials, pigmenting agents, inks, and degradation products resulting from parchment-environment interactions, not only offers valuable insights into the provenance and dating but also constitutes a fundamental pre-requisite in view of the development of proper intervention strategies to be applied. Moreover, another important task in dealing with ancient parchments regards the employment of various disinfection methods aimed at safeguarding parchment artifacts against bio-deterioration, in order to promptly suppress any ongoing microbial activity originating from bacteria and fungi [4]. This aspect turns out to be particularly active in collagen-based materials, which act as nutrient-rich medium for microbial growth, colonizing the document surface even upon unfavorable temperature and humidity conditions.

In the light of the aforementioned considerations, this paper reports some preliminary results of a non-invasive multi-technique investigation on a written illuminated parchment dating back to the XVII century, belonging to the *S. Maria di Montalto* Church (Messina, Italy), by employing X-ray Fluorescence (XRF) spectroscopy, micro-Raman spectroscopy and Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance Geometry (FTIR-ATR). Starting from the elemental and molecular composition of both blank and decorated areas, information about the artist's manufacturing technique, typical of a specific "school" or period, was retrieved, allowing the possibility to verify its authenticity and hypothesize the origins of the artistic methods tracing potential influences or cross-regional exchanges in stylistic practices. Finally, the recognition of degradation markers and alteration products shed light into the current state of conservation of the parchment, guiding the selection of suitable conservation interventions for its sustainable preservation and valorisation.

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 archival 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 Mathematics 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'.

II. MATERIALS AND METHODS

A. The parchment

The investigated parchment, known as "*V.R.B.S. Messina Nobilis...*", consists of a single sheet of ~ 530 × 295 mm decorated on both the *recto* and *verso* side, belonging to the archive material of the *S. Maria di Montalto* Church (Messina, Italy). In this preliminary work we focused our attention only on the *recto* side (Figure 1), consisting of a written page with dark text, placed within a frame characterized by reddish and blue floral decorations enclosed by two red boxes. Four globes placed on each side can be distinguished, together with noticeable gold decorations for the realization of some capital letters.

In particular, we selected 17 points (labelled as R#, with # = 1,…, 17) for XRF, µ-Raman and FTIR-ATR analyses, trying to investigate both the background layer and the different colors/tonalities used for decorations.

B. X-ray Fluorescence (XRF) measurements

XRF measurements have been performed through a portable XRF "Alpha 4000" (Innov-X systems, Inc., Woburn, MA, USA) instrument, enabling the detection of chemical elements with an atomic number (Z) between phosphorus and lead. The apparatus is equipped with a Ta anode X-ray tube as the source and a Si PIN diode (active area of 170 mm^2) as the detector. For each area, two sequential tests were carried out with operating conditions of 40 kV and 7 µA and 15 kV and 5 µA for the first and second run respectively, for 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.

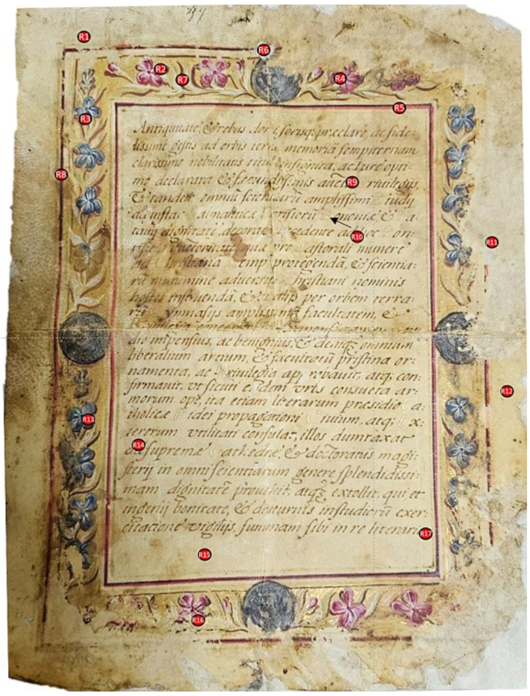

Fig. 1. Recto of the "V.R.B.S. Messina Nobilis…" parchment after restoration, with the position of the analysed areas indicated.

C. Micro-Raman measurements

Micro-Raman measurements were performed using a portable Raman "BTR 111 Mini-Ram TM" (B&W Tek, Inc., Newark, NJ, USA) spectrometer. The instrument is equipped 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 recorded in the range 62–3150 cm^{-1} with a resolution of 10 cm^{-1} and an acquisition time of 10 s × 32 scans. Calibration was performed using the silicon chip peak at 520.6 cm^{-1}, ensuring optimal instrument performance. The system includes a BAC151B Raman microscope with an 80× objective which guarantee a working distance of 1.25 mm, and a laser beam spot size of 25 µm. The laser maximum power delivered to the samples was ~ 60 mW. Band assignment was carried out by comparing the experimental spectra with data reported in various databases and the literature [5,6].

D. FTIR-ATR measurements

FTIR-ATR Data were recorded in the 400–4000 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. When working in ATR geometry, the evanescent wave is attenuated in that region of the IR spectrum where the sample absorbs energy. A resolution of 4 cm^{-1} was used, by adding 100 repetitive scans, in order to guarantee a good signal-to-noise ratio and highly reproducible spectra. The obtained IR spectra were properly normalized for taking into account the effective number of absorbers. No smoothing was done, and the data manipulations such as baseline adjustment and normalization were performed using the Spectracalc software package GRAMS (Galactic Industries, Salem, NH, USA).

III. RESULTS AND DISCUSSION

Figure 2 reports the XRF, micro-Raman and FTIR-ATR spectra collected on points R11, R12 and R15, representative of undecorated areas of the *recto* of the parchment. XRF results (see Figure 2a) highlight the presence of calcium (Ca), likely attributable to the calcination process, alongside with traces of iron (Fe), zinc (Zn), and arsenic (As). The absence of a major component suggests a primarily organic composition, with minor contributions presumably originating from external contamination and/or materials introduced during manufacturing process. Regarding the molecular composition, micro-Raman spectra (see Figure 2b) acquired at corresponding points revealed the presence of organic compounds and calcite ($CaCO_3$), a residue consistent with the calcination treatment. Complementarily, FTIR-ATR analysis has enabled us to unambiguously identify the use of collagen, a fibrous protein characteristic of the animal connective tissue, suggesting that the writing support is derived from animal skin. More in details, a measure of the FTIR-ATR intensity ratio between the primary (A_I) and secondary (A_{II}) amide bands (A_I/A_{II}) of collagen (see Figure 2c), along with their relative frequency-centre gap, provided insights into the degradation state of such fibrous matrix, potentially induced by hydrolysis or gelatinization processes. Specifically, considering that, with the exception of R12, the A_I/A_{II} ratio is approximately 0.96, it can be inferred that the fibrous structure largely retains its original integrity, thus indicating a good structural state of the collagen-based parchment support. Finally, the absence of significant spectral contributions around ~1740 cm^{-1} indicates minimal or absent oxidative degradation.

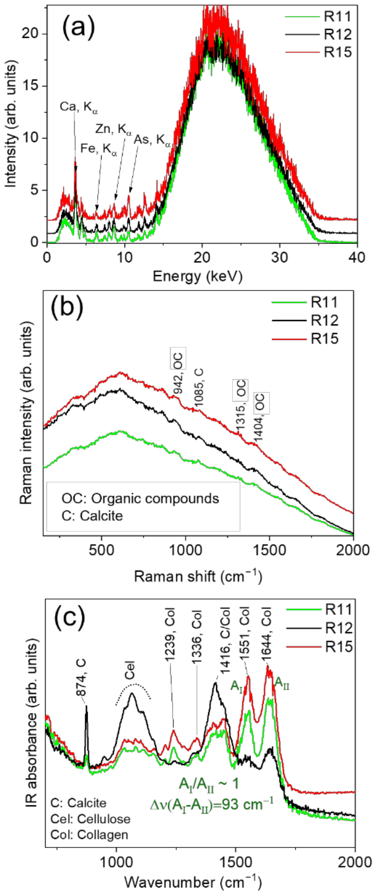

Fig. 2. (**a**) XRF, (**b**) micro-Raman and (**c**) FTIR-ATR spectra collected on points R11, R12, and R15.

Interestingly, only for point R12, the presence of the typical FTIR-ATR features associated to cellulose can be distinguished, most likely associated with the application of methylcellulose ($C_{20}H_{38}O_{11}$) during restoration interventions.

Concerning the red-colored areas of the parchement, Figure 3 shows the XRF (Figure 3a) and micro-Raman (Figures 3b,c) spectra collected on two areas, *i.e.* points R4 and R7, representative of the floral decorations present around the text of the *recto*.

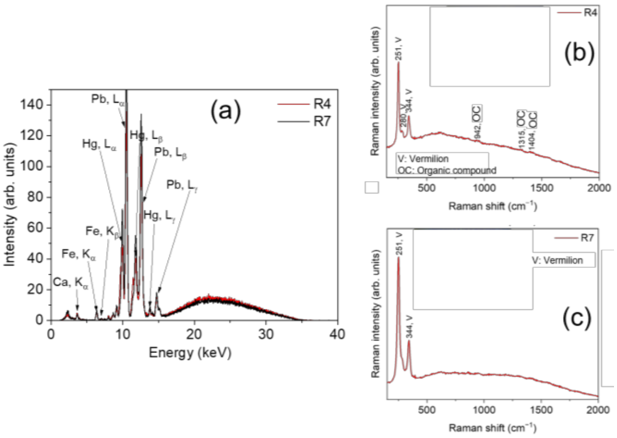

Fig. 3. XRF (**a**) and (**b,c**) micro-Raman spectra collected on points R4 and R7.

The elemental analysis revealed the presence of mercury (Hg), from the observation of its characteristic lines centered at ~ 9.98 keV (L_α transition), ~ 11.82 keV (L_β transition) and ~ 13.83 keV (L_γ transition), suggesting the use of vermillion (HgS) for the red/brown decorations. In addition, the presence of lead (Pb) can be attributed to the use of a Pb-based compound, reasonably lead white, used as preparatory layer for the color, or deriving from contamination deposited on the surface layer due to the employment of tools for sanding the parchment surface. Moving to the molecular characterization, the collected micro-Raman spectra allowed us to confirm - by observing the corresponding characteristic bands [5,6] - the use of vermilion (HgS) for the realization of red/reddish areas, together with contributions arising from organic components presumably related with the underlying membrane. Notably, for point R16 (spectrum not shown), beside vermilion and organic contributions, an additional band at ~ 615 cm⁻¹ can be distinguished, suggesting the presence of iron oxides [5].

As far as the blue color is concerned, Figure 4 shows, as example, the XRF, micro-Raman and FTIR-ATR spectrum collected on a bluish floral motif placed in the text outline (point R3), representative of blue decorations of the parchment. Although the elemental analysis did not reveal any chromophore element - only Hg attributable to the surrounding red decorations, Pb arising from the underlying layer, and traces of Ca and Fe - the micro-Raman spectrum (Figure 4b) enabled the identification of diopside, a naturally occurring mineral contaminant in lapis lazuli. In particular, prismatic diopside crystals incorporating transition metals give rise to the characteristic spectral features observed between approximately 1100 and 2000 cm⁻¹, which cannot be ascribed directly to lazurite (the principal mineral constituent of lapis lazuli, $Na_3Ca[Al_3Si_3O_{12}]S$). Notably, the presence of this spectral feature not only confirms the use of a ultramarine blue pigment derived from a natural source, but also provides valuable information regarding the pigment's provenance, in agreement with [7]. It is worth of note that our results are consistent with the approach reported in [7], as the combined vibrational and compositional analyses likewise reveal diagnostic features of the ultramarine matrix and accessory minerals, thereby reinforcing the interpretative framework for disentangling the mineralogical complexity of lapis lazuli pigments and for linking their properties to geological sources.

Such aspect is further corroborated by the FTIR-ATR spectrum (Figure 4c), which revealed the typical ultramarine blue large absorption band at ~ 1000 cm⁻¹, accompanied by features associated to calcite and arabic gum, the latter employed as a binding medium for the pigment [6].

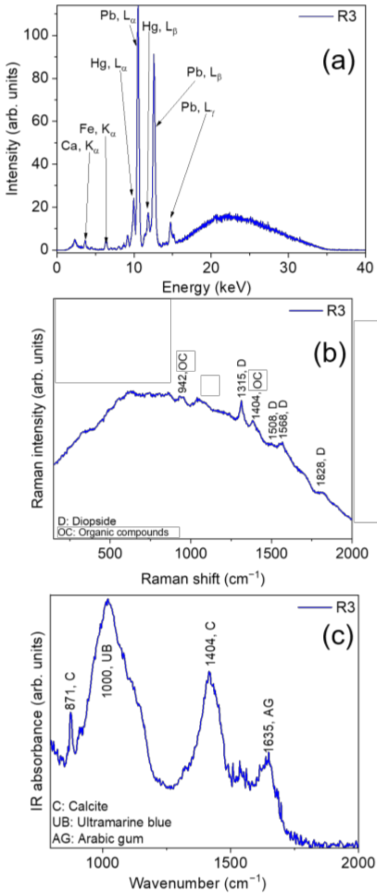

Fig. 4. (**a**) XRF, (**b**) micro-Raman and (**c**) FTIR-ATR spectrum collected on point R3 of the recto of the parchment.

Finally, with regard to the composition of the ink, Figure 5 presents the comparison of the XRF, micro-Raman and

FTIR-ATR spectra collected on a “dark” and “golden” letter within the text on the *recto* of the parchment (points R9 and R10, respectively). Concerning point R9, XRF analysis (Figure 5a) revealed high amount of Pb - likely originating from the underlying layer or contamination - along with minor content of Ca and Fe. In contrast, the elemental composition of the golden letter (point R10) shows, in addition to the aforementioned elements, a significant concentration of gold (Au), presumably resulting from the application of gold leaf or gold powder, suggesting a refined artistic technique and high commissioning of the artist. Micro-Raman analysis allowed for the identification, in point R9, of an organic component presumably attributable to carbon black, along with calcium oxalates [5,6]. Concerning point R10, the molecular composition additionally includes a metallic component, as evidenced by the presence of a low-frequency spectral feature, likely associated with a thin gold layer deposition.

Finally, FTIR-ATR analysis confirmed, for the black letter (i.e., R9), the presence of a carbon-based black pigment, presumably used as ink, along with arabic gum as a binding medium, calcite from the underlying layer, and calcium oxalates.

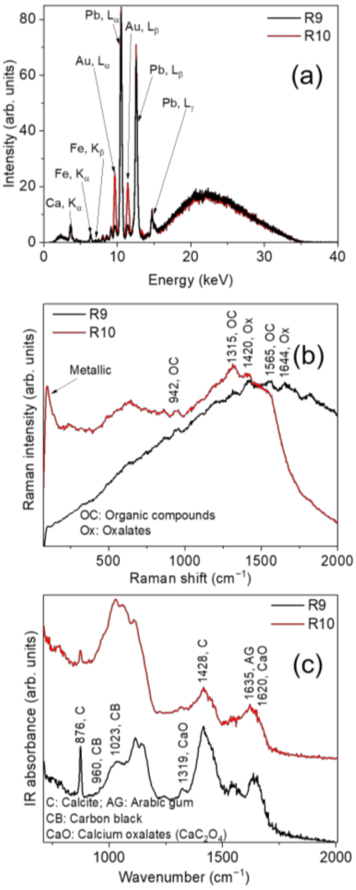

Fig. 5. Comparison of the (**a**) XRF, (**b**) micro-Raman, and (**c**) FTIR-ATR spectra collected from points R9 and R10, corresponding to the “dark” and “golden” letters, respectively.

For all the investigated points, an overview of the main hypotheses regarding the used pigments and other materials, deduced from the analyses carried out in the work, is reported in Table 1.

Table 1. Investigated point, summarized according to the color of analyzed pigments, together with the main hypotheses regarding the used pigments and other materials deduced from all the analyses carried out in the work.

Point of Analysis	**Color**	**Used Pigments and Other Materials**
R3	Blue	Ultramarine, calcite, arabic gum
R4, R7	Red	Vermilion, iron oxides, Pb-based compounds
R9	Black	C-based compounds, arabic gum, calcite, calcium oxalates
R10	Yellow	Gold leaf/gold powder, arabic gum, calcite, calcium oxalates
R11, R12, R13	undecorated	Collagen, cellulose, calcite

IV. CONCLUSIONS

In the present paper, a non-invasive multi-technique investigation was performed on a XVII century illuminated parchment belonging to the *S. Maria di Montalto* Church in Messina, Italy. In particular, the simultaneous employment of X-ray fluorescence (XRF) spectrometry, μ-Raman spectroscopy and Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance geometry (FTIR-ATR) allowed us to successfully characterize, both at the elemental and molecular scales, the composition of the raw materials used by the artist both in terms of preparatory components and pigmenting agents. Results highlighted the use of compounds characteristic of the historical context, implying considerable artistic and economic value of the artefact, deduced from the thoughtful use of rare and expensive pigments and gilding. It is worth of note that obtained information not only contributed to the enhancement of cultural assets but also provided, through non-invasive approaches, a solid basis for future conservation strategies to be applied. An extension of the analysis to a larger set of points, as well as a detailed microbiological survey, will be addressed in the future, not only for a more comprehensive understanding of the material composition and execution technique, but also for the development of optimized strategies to protect parchment artifacts from biodeterioration.

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