2023 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
Rome, Italy, October 19-21, 2023

Unveiling Hidden Insights of Ancient Roman wall paintings in Cremona: In-Depth Knowledge Beyond the Surface with Spectroscopic Analysis

Francesca Volpi*[1,2], Michela Albano[1,2], Chiara Delledonne[2], Giacomo Fiocco[1,2], Chaehoon Lee[3,2], Marco Malagodi[1,2], Maduka Lankani Weththimuni[3]

[1] *Department of Musicology and Cultural Heritage, University of Pavia, Corso Garibaldi 178, 26100 Cremona, Italy, francesca.volpi@unipv.it*, michela.albano@unipv.it, giacomo.fiocco@unipv.it, marco.malagodi@unipv.it*
[2] *Arvedi Laboratory of Non-Invasive Diagnostics, CISRiC, University of Pavia, Via Bell'Aspa 3, 26100 Cremona, Italy*
[3] *Department of Chemistry, University of Pavia, Via Torquato Taramelli 12, 27100 Pavia, Italy, chaehoon.lee1@universitadipavia.it, madukalankani.weththimuni@unipv.it*

***Abstract* – This research represents the first non-invasive analytical study on the wall paintings of the *Domus del Ninfeo* (1st century B.C.) excavated in Cremona. Scientific analysis played a crucial role in investigating the pigments and the painting technique and contributed to a deeper understanding of one of the provinces of ancient Rome in Northern Italy. To this aim we utilized portable X-ray fluorescence (XRF) combined with FTIR spectroscopy in external reflection mode (ER-FTIR) for characterizing the wall decorations. The outcomes revealed that wall paintings were executed using the fresco technique, employing costly pigments such as Egyptian blue for blue and green shades, and cinnabar for vibrant red and pink hues. These expensive pigments were sometimes mixed with more common pigments like green earth and red ochre, while calcium carbonate was used for white tones and lighting effects. Overall, this research deepened our understanding of the artistic practices and connections between coeval societies of the Roman Empire.**

Keywords – non-invasive analysis, ER-FTIR, XRF, wall painting, pigments

I. INTRODUCTION

During the excavations conducted between 2005 and 2008 in Cremona (Northern Italy) hundreds of fragments of wall paintings were discovered from the *Domus del Ninfeo*, a private residence dated back to ca. 35-34 B.C. which was destroyed in 69 A.D. by Vespasian's troops. After laborious conservation and reconstruction works coordinated by the San Lorenzo Archaeological Museum in Cremona, the finds have made it possible to reconstruct part of the figurative representations of the walls of the *domus*, where the ancient myth of Ariadne was depicted. The finesse of the execution and the richness of the iconographic themes and motifs suggested the commissioning of high-ranked social figures who shared the tastes and customs in vogue in Rome at that time [1]. Beyond the stylistic evidence, the role of scientific analysis has been central in investigating the materials used and attempting to reconstruct the relationships with the coeval Roman society in central Italy (e.g., Rome, Ostia, Pompeii).

Nowadays, the diagnostic approach for the study of art materials is increasingly focused on completely non-invasive and portable techniques that allow analysis from the surface of the sample without damaging it and without the need for sampling. Among these techniques X-ray fluorescence and Raman spectroscopies have provided significant improvements in the rapid and reliable discrimination of materials with different chemical composition and pigments characterization [2-3]. In the past decade, within the class of spectroscopic techniques, highly informative analytical results have often been obtained through portable Fourier Transform Infrared (FTIR) spectrometers working in reflection modes, such as fiber optic or external reflection configurations, which combine the advantages of portability with those of non-invasive, reproducible, and sensitive analysis [4]. However, despite the increase in the use of reflection IR techniques, there are still challenging aspects to interpreting spectra, and therefore acquisition of spectral databases is often necessary to interpret signals and attribute bands.

Aimed at identifying the execution painting technique and pigments used in wall decorations of the *Domus del Ninfeo* non-invasive multi-analytical measurements were carried out on a selection of fragments of representative colors. The tailored analytical methodology included portable instruments: X-ray fluorescence (XRF) and FTIR spectroscopy in external reflection mode (ER-FTIR). The data acquired with the two instruments were then combined to provide complete and comprehensive information about the pictorial layers, such as the identification of pigments and the presence of organic binder or patinas. It is worth mentioning that this is the first non-invasive analytical study conducted on the wall painting decorations of the Roman *domus* in Cremona, and it proved relevant to deepening knowledge about one of the provinces of ancient Rome located in northern Italy. An additional novelty of the study is the application of portable ER-FTIR working between 7500 and 360 cm^{-1}, as complementary technique to XRF analysis, enabling the identification and discrimination of different pigments within the same chemical class.

II. EXPERIMENTAL

A. XRF

A portable energy-dispersive spectrometer ELIO (XG Lab, Milan, Italy; Bruker Optics, Billerica, MA, USA) equipped with a rhodium (Rh) anode, a Silicon Drift Detector (SDD), and a beam collimated to the sample surface with a spot diameter of about 1.3 mm was used. Measurements were performed at 40 kV tube voltage, 40 µA tube current for 120 s, and 2048 acquisition channels. Data were processed by ELIO 1.6.0.29 software.

B. ER-FTIR

A portable Alpha spectrometer (Bruker Optics, Etringen, Germany; Billerica, MA, USA) equipped with a SiC globar source, a permanently aligned RockSolid interferometer with gold mirrors, and a DLaTGS detector was used. Measurements were performed in external reflection mode with a 23°/23° optical layout, with a diameter of 3 mm. Analyses were carried out in the range 7500-360 cm^{-1} with a spectral resolution of 4 cm^{-1}. For each point 145 spectra (3 min scan time) were acquired, averaged, and transformed in log(1/R) (R = reflectance) by OPUS 7.2 software package. A gold flat mirror was used as background.

Figure 1 *represents the ancient roman fragments from the wall decorations of the Domus del Ninfeo in Cremona analyzed in this work.*

C. The Domus del Ninfeo

The *Domus* resulted in several rooms with multiple polychromatic decorations on the walls depicting geometric, floral, and mythological motifs. Among the colorful decorations fragments of blue, green, red, and white color (Figure 1) were considered significant to investigate the palette in use at that time in the Cremona's *domus* by XRF and ER-FTIR used as complementary techniques.

III. RESULTS

Results of the analytical investigation on the decoration of the *domus* are reported and discussed below.

A. Blue and green

Fragments 19-B and 19-G come both from wall decoration depicting the epiphany of Dionysus to Ariadne. The two fragments show slightly different colors with a light-blue and a green hue, respectively, and the combination of XRF and ER-FTIR data permitted the identification of the specific chromophores responsible for the color. In order of abundance, the principal elements revealed by XRF in fragment 19-B were calcium (Ca), copper (Cu), strontium (Sr), and iron (Fe) followed by lower counts of potassium (K) and silicon (Si). While Ca and Sr are mainly due to the plaster, Cu implies the use of a copper-based pigment, and Fe and K suggested lower amount of an earth pigment. The acquisition of ER-FTIR analyses on the same fragment, reported in Figure 2-a, was crucial for attributing the presence of copper to Egyptian blue ($CaOCuO(SiO_2)_4$) through the diagnostic inverted bands of Si-O stretching at 1165, 1074, 1005 cm^{-1}, combination bands of silicates at 1980 and 1877 cm^{-1} and inverted bands in the lower wavenumbers region (665, 525, 480, 420 cm^{-1}) [5]. The finding of Egyptian blue rather than other less expensive blue pigments provided support for the hypothesis that the decorations in the *domus* were commissioned by wealthy, high-ranking owners. In fact, the production of Egyptian blue, obtained by heating a mixture of calcite, siliceous sand, copper compounds, and natron or plant ash, to a temperature ranging between 850 and 950°C, made this pigment one of the most expensive at that time.

Investigations carried out on fragment 19-G revealed the same chemical elements of 19-B but in a different order of abundance. The most abundant element was Ca followed by Fe, K, and lower counts of Cu, Sr and Si, suggesting the application of mainly a green earth pigment and lower amounts of Egyptian blue. ER-FTIR analyses confirmed this hypothesis and identified the presence of celadonite, a green chromophore mineral belonging to the mica group found in green earths. It is worth highlighting that the two main green clay minerals of green earth pigment are celadonite $K(MgFe^{2+})(Fe^{3+}, Al)Si_4O_{10}(OH)_2$ and glauconite $(K, Na)(Fe^{3+}, Al, Mg)_2 (Si, Al)_4O_{10}(OH)_2$. Despite to the similar chemical composition of the two minerals they have different formation environments: celadonite comes from the alteration of basaltic igneous rocks found in some areas with volcanic activity, while glauconite clays have sedimentary geological origin [6]. In fragment 19-G (Figure 2-b) celadonite was identified by the combination bands of OH in the NIR region, the OH stretching between 3600 and 3535 cm^{-1}, and the sharp Si-O bending peaks below 600 cm^{-1} [7]. In this regard the ability of identify celadonite in blue and green decorations of Cremona's *domus* using non-invasive and portable ER-FTIR, as complement technique for XRF, was important to get insights on a possible source of the raw pigment. Indeed, it could be hypothesized that the green earth had origin from caves near Verona (Northen Italy), mainly constituted by celadonite [7].

B. Red and pink

The red color was the most used in the decorations of the *domus*. The fragments here analyzed and representing different hues and shades of red are 15-R and 12-R in Figure 1. The first derived from a background decoration of a wall of the *domus* which was homogenously painted with a red vivid color. The same hue was found in many fragments constituting a large painted portion of the wall. Fragment 12-R, instead, consisted of two well-defined shades of dark and light red, namely red and pink color. The analysis of chemical elements carried out on 15-R by XRF (Figure 3-a) revealed the following relative order of abundance: mercury (Hg) > sulfur (S) > Ca, followed by lower counts of Fe, Sr, and Si. This results in the clear determination of cinnabar (HgS) as the predominant pigment. The counts of S were significantly high even though light elements result underestimated under our working conditions [8] implying a considerable abundance of this pigment. The presence of Ca and Sr is due to the lime mortar of the painting, while Fe may suggest the addition of a red ochre (or other iron-based pigment) in mixture with cinnabar, as previously reported in another study [9].

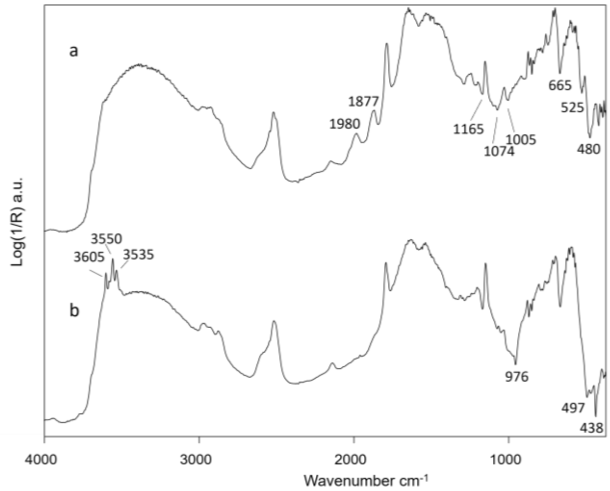

***Figure 2** reports the ER-FTIR spectra of the blue fragment 19-B (a), and green 19-G (b).*

The identification of cinnabar was not surprising due to the fact that it was certainly among the most important and characteristic pigments in ancient roman painting. However, cinnabar was also the most expensive pigment and its use for large decorations provided further strength to the hypothesis of the high social rank of the inhabitants of the *domus*, who were very close to the aesthetic and artistic taste of Imperial Rome.

Differently, the dark area of fragment 12-R in Figure 3-b was mainly constituted by the following chemical elements: Ca > Fe > Hg, along with the minor elements Sr, S, Si. This difference with fragment 15-R suggested a mixture of an iron-based pigment, possibly a red ochre, with cinnabar to achieve a dark red hue. The application of these pigments in overlapped layers cannot be excluded either, but in this case the application of non-invasive techniques cannot determine whether the pigments were mixed or overlapped.

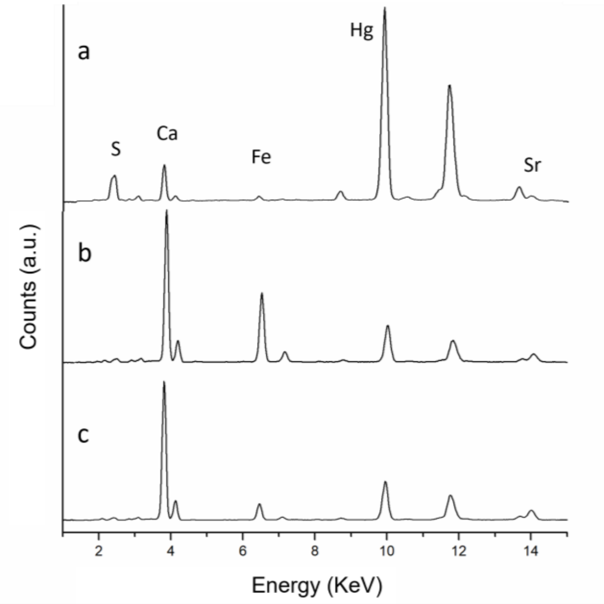

Figure 3 *reports the XRF spectra of reds fragments: 15-R (a), 12-R dark red (b) and pink (c) areas.*

The pink area of fragment 12-R showed in figure 3-c interesting differences in the counts of major elements: Ca and Hg were statistically higher than those of dark red, while Fe lower. This result suggests that cinnabar was possibly mixed with a lower content of red ochre and a large amount of calcium carbonate to obtain a pink bright hue. In accordance with XRF results, ER-FTIR spectra acquired in fragment 12-R, both on dark red and pink areas, revealed the signals of hematite by its diagnostic inverted bands around 530 and 470 cm^{-1} (Fe-O stretching) [10]. The two bands were more intense in the dark red color than pink. In addition, thanks to the range of detection reaching as far as a portion of the far-IR region a different spectral feature was evidenced in fragment 12-R in comparison with 15-R, where in the latter an increase of the signal at the edge of the detector range was related to cinnabar that shows characteristic absorption below 360 cm^{-1}.

C. White

The elemental composition of fragment 13-W resulted by XRF in the highest counts of Ca detected so far, followed by Fe, Sr, and not negligible counts of K and Si. In accordance with this data, ER-FTIR detected calcium carbonate bands at 4270, 2515, 2145, 1960, 1795 cm^{-1} (for overtones and combination bands), 1410, 875 and 711 cm^{-1} (belonging to CO_3^{2-} stretching and bending vibrations), together with those of silicates around 1000 cm^{-1} [8]. Hematite vibrations of Fe-O bonds were also recognized around 530 and 470 cm^{-1} [11]. In this case, the presence of iron compounds was interpreted as intentionally added in little portion to calcium carbonate to achieve a slightly pale pink color. These results, however, are consistent with other studies of white pigments used in ancient Roman wall paintings [12].

D. Painting technique

Both XRF and ER-FTIR results accordingly confirmed calcium carbonate as the binder for the wall painting surface of the *domus*. Calcium was the most abundant element detected by XRF in all the fragments but 15-R. Moreover, the ubiquitous presence of Ca and Sr, where the latter is generally vicarious of calcium, along with the ER-FITR diagnostic bands of carbonate around 4270, 2515, 2145, 1795, 1410 cm^{-1} implies that the wall decorations were executed with the fresco technique. A more detailed observation of the ER-FTIR spectra revealed that in addition to the carbonate ion bending at 874 and 712 cm^{-1}, signals around 855 and 730 cm^{-1} suggested the presence of other carbonate than calcium carbonate, possibly dolomite, a calcium and magnesium carbonate which was revealed in other Roman wall paintings.

Only in fragment 15-R calcium was not the most abundant element; interestingly, reflection spectra showed a signal around 1733 cm^{-1} which may suggest the presence of an organic binder containing a C=O bonds, e.g. lipidic binder. Although the find may suggest the use of “a secco” technique, the lack of other clear bands related to this possible binder along with the overlap with multiple bands due to carbonate in the middle-IR region prevented further discussion of the signal.

IV. CONCLUSIONS

In this study we presented the results of the first analytical investigation carried out on the wall paintings of the *Domus* del Ninfeo (1st century B.C.) discovered in Cremona during archaeological excavations in 2005-2008. It offered the opportunity to determine the chemical and sometimes mineralogical composition of the pigments and the painting technique used by the Roman artists working in Cremona, and to compare them with those in central Italy at that time.

The non-invasive approach used in this research combined elemental and molecular spectroscopy, namely XRF and ER-FTIR, to provide an effective, rapid, and reliable method for a complementary characterization of the materials used to decorate the *domus* surfaces. Results achieved so far suggested that the wall paintings were mainly made by a fresco technique in which lime slake was used as binder, successively transformed by carbonation. Egyptian blue and green earth were identified in light blue and green decorations, while cinnabar and red ochre in reds with different shades and hues. The use of ER-FTIR in combination with XRF has been crucial in specifically determining Egyptian blue and celadonite, the latter as chromophore of green earth, providing possible insights into the reconstruction of links and trades between coeval societies within the Roman Empire.

The identification of these pigments not only was consistent with those largely found in wall paintings of Central Italy at that time, but also confirm the richness and fine executions of the pictorial decorations of the *domus* of Cremona.

ACKNOWLEDGEMENTS

We are grateful to Elena Mariani (Archelogist specialized in Roman Frescos), Marina Volonté (Museum Conservator at the Archaeological Museum "San Lorenzo" in Cremona), and Dr. Nicoletta Cecchini (Soprintendenza Archeologia, Belle Arti e Paesaggio per le province di Cremona, Lodi e Mantova) for authorizing and supporting the study of the Roman fresco samples.

REFERENCES

[1] E. Mariani, N. Cecchini, M. Volontè, "Pictura tacitum poema. Miti e paesaggi dipinti nelle domus di Cremona", ISBN 9788878491830, Ante Quem, Cremona, 2023.

[2] F. Pozzi, A. Rizzo, E. Basso, et al., "Portable spectroscopy for Cultural Heritage" in: Crocombe R, Leary P, Kammrath B, eds. Portable Spectroscopy and Spectrometry, Wiley, 2021 pp. 499-522.

[3] A. Rousaki, P. Vandenabeele, "In situ Raman spectroscopy for cultural heritage studies", J. Raman Spectrosc., Vol.52, 2021, pp. 2178-2189.

[4] C. Miliani, F. Rosi, G. Brunetti, A. Sgamellotti, "In situ non-invasive study of artworks: the MOLAB multitechnique approach", Acc. Chem. Res., Vol.43, No.6, June 2010, pp. 728-738.

[5] P. Baraldi, F. Bondioli, C. Fagnano, A.M. Ferrari, A. Tinti, M. Vinella, "Study of the vibrational spectrum of cuprorivaite", Ann. Chim., Vol.91, No.11, 2001, pp. 679-692.

[6] N. Eastaugh, "Pigment Compendium: A Dictionary and Optical Microscopy of Historical Pigments", Routledge, 2008.

[7] F. Ospitali, D. Bersani, G. Di Lonardo, P.P Lottici, "Green earths: vibrational and elemental characterization of glauconites, celadonites and historical pigments" J. Raman Spectrosc., Vol.39, 2008, pp. 1066-1073.

[8] F. Volpi., G. Fiocco, T. Rovetta, et al., "New Insights on the Stradivari *Coristo* Mandolin: A Combined Non-Invasive Spectroscopic Approach", Appl. Sci., Vol.11, 2021, pp. 1-11.

[9] M.L. Amadori, S. Barcelli, F. Ferrucci, G. Poldi, "Invasive and non-invasive analyses for knowledge and conservation of Roman wall paintings of the Villa of the Papyri in Herculaneum", Microchem. J., Vol.118, 2015, pp. 183-192.

[10] F. Volpi, M. Vagnini, R. Vivani, M. Malagodi, G. Fiocco, "Non-invasive identification of red and yellow oxide and sulfide pigments in wall-paintings with portable ER-FTIR spectroscopy", J. Cult. Herit., Vol.63, 2023, pp. 158-168.

[11] G. Fiocco, M. Albano, C.Merlo, T. Rovetta, C. Lee, F. Volpi, A. Bergomi, C.A. Pini, C.A. Lombardi, C. Mariani, V. Comite, M. Malagodi, P. Fermo, V. Guglielmi, "Non-invasive characterization of Bernardino Luini's color palette: a spectroscopic campaign on the frescos of Santuario della Beata Vergine dei Miracoli in Saronno (Italy)" Proc. of 2022 IMEKO TC-4 International Conference on Metrology for Archaeology and Cultural Heritage, 2022.

[12] R.M Ion, M.G. Barbu, A. Gonciar, G. Vasilievici, A.I. Gheboianu, S. Slamnoiu-Teodorescu, M.E. David, L. Iancu, R.M.A Grigorescu, "Multi-Analytical Investigation of Roman Frescoes from Rapoltu Mare (Romania)", Coatings, Vol.12, No.530, 2022, pp. 1-19.