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# "Analyzing an Ancient City: Non-invasive studies of Ostia Antica Archaeological Park's Wall Paintings"

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***Abstract –***
**Roman wall paintings at the archaeological site of Ostia Antica dating from the 1st century BCE to the 4th century CE were studied in an integrated non-invasive approach using portable instrumentation, namely: Nuclear Magnetic Resonance (NMR), Hyperspectral Imaging (HSI), X-ray fluorescence (XRF), Visible Induced Luminescence (VIL), External Reflectance Fourier-Transformed Infrared Spectroscopy (ER-FTIR), Raman and Near Infrared (NIR) Spectroscopies. The objective of this study is threefold: to investigate the materials and techniques of wall paintings at Ostia Antica in order to gain insight into the evolution of the use of materials and painting techniques over time, the testing of novel instrumentation in archaeological contexts such as portable HSI and the recently developed NMR hardware and stratigraphy protocols, as well as to aid in the conservation efforts at the site by providing information on the material composition of the walls. Some of the main results of four campaigns dating 2019-2023 are presented.**

**Keywords**: NMR, XRF, ER-FTIR, NIR, Raman, Hyperspectral imaging (HSI), remote sensing, mural paintings, VNIR-SWIR reflectance spectroscopy, VIL, SmART_scan pigments mapping.

## I. Introduction

Ostia Antica was the harbor city of Rome during Antiquity. Located at the mouth of the Tiber River, it was born as a military settlement to protect the capital of the Roman Empire, and control trade across the sea but it quickly became a large and rich city, the maritime façade of Rome and the door to the Empire. Today, Ostia is one of the largest archaeological sites in Italy, which unlike Pompeii or Herculaneum, preserves buildings phases spanning almost a millennium, from the 4th c. BCE to the 6th c. CE, with seven centuries of wall painting history, from the second century BCE to the fifth century CE. This makes Ostia Antica an unequal site to investigate the evolution of ancient painting through time from the Republic era to Late Antiquity. However, the scientific studies of Ostia's wall paintings have been scarce and mainly performed on selected samples. The present study aims to characterize a large number of Ostia's wall paintings, in situ and in fragments, through a non-invasive, multi-analytical approach. Along with the application of routine methods of analysis such as XRF, Raman, NIR, and FTIR, the exploration of novel portable analytical instrumentation such as HSI, and improved portable NMR and the newly developed SmART_Scan mapping software is also an aim of this study. Moreover, the information obtained throughout these investigations aids the site preservation efforts by shedding light on the presence of early undocumented conservation treatments along with providing information on the materials and pigments composition of the walls which ultimately assists in the design of conservation strategies for the paintings. See Table 1 in the Appendix for a summary of the techniques used. Archaeologists and conservators, working alongside scientists, create a model for future multidisciplinary collaborations at other archaeological sites. This project is the first one of its kind to be carried out on such a large and widespread scale in Ostia.

## II. Materials and Methods

Wall paintings found within fourteen different buildings constructed throughout five centuries (1st century BCE to 4th century CE) have been analyzed. The summary of the results is described below.

### A. NMR stratigraphy

The mortar-layer stratigraphy of Roman wall paintings at Ostia Antica was studied on two occasions with nuclear magnetic resonance (NMR) depth profiling [1] in combination with portable X-ray fluorescence (XRF), and visible induced luminescence (VIL) to explore manufacturing details in the context of the use and history of the buildings. In the first campaign in 2019 the NMR signature of covered wall paintings was studied for the first time [2], while in the second campaign in 2022, depth profiles were compared to answer the question if different painted walls were prepared for painting at the same time or by the same workshop [3]. Moreover, the experience gained

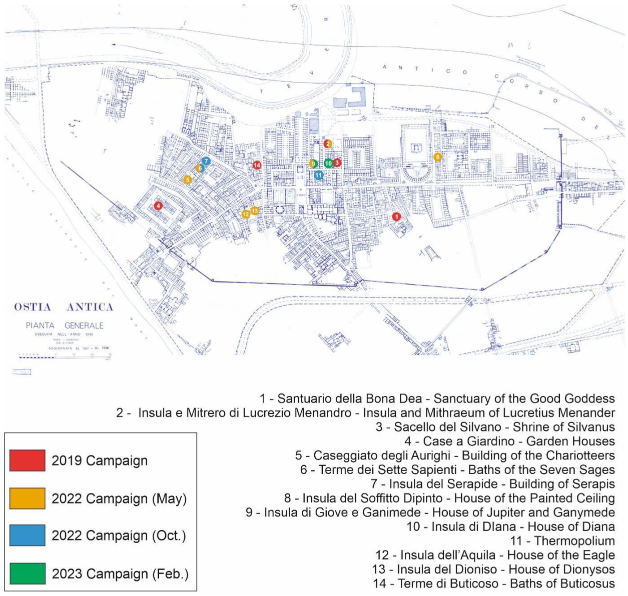


*Figure 1. Map of Ostia Antica showing the different buildings studied in 2019 (red), May 2022 (yellow), October 2022 (blue), and 2023 (green).*

depth profiles were compared to answer the question whether different painted walls were prepared for painting at the same time or by the same workshop [3]. Moreover, the experience gained in handling the portable NMR hardware for onsite measurements has stimulated the development of an improved NMR depth-profiling instrument [4].

*Figure 2. Setup of the NMR-MOUSE when measuring a depth profile into a painted wall in the Mitreo di Lucrezio Menandro. The sensor with a strong magnet rests on a displacement stage on top of a scaffold close to the wall for point-by-point acquisition of a depth profile.*

The experimental results from the two measurement campaigns are summarized, and progress of the ongoing project to improve the NMR depth-profiling equipment (Fig. 2) is reported. An example of such results can be seen in Figure 3 below which shows the NMR results obtained at the Cassegiato del Dionisio. The depth profiles A and B are similar. The profile from wall C is somewhat different, but this wall has been covered with lichen. While the signatures of the mortar layers below 7 mm are similar for spots A and C, the top layers differ somewhat. This suggests that wall C has been plastered with the same technique but by a crew different from that working on walls A and B.

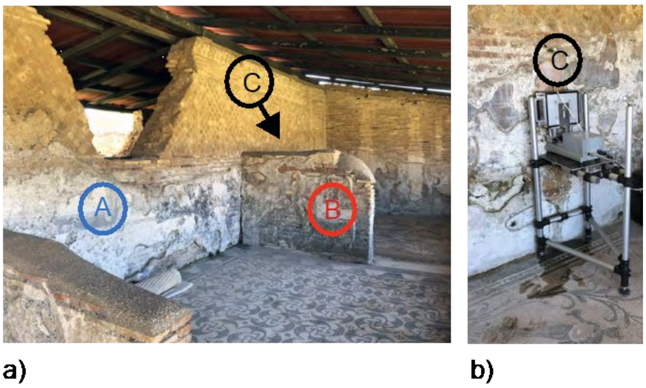


*Figure 3. NMR. Cassegiato del Dionisio. a) Positions where NMR Depth profiles were measured. b) Setup for NMR-Depth profiling showing the NMR-MOUSE on a scaffold. c) NMR depth profiles.*

### *A. Hyper-Spectral Imaging (HSI)*

Hyper-Spectral Imaging (HSI) is a well-established technique, which is profitably used in the CH field for non-invasive diagnostics and documentation of polychrome surfaces (paintings, manuscripts, etc.). Besides the well-rooted applications in museum contexts, recently remote-sensing approach has been proposed to extend HSI applications outdoors, including the archaeological sites. In particular, pioneer HSI campaigns previously carried out in the Pompeii site by using readapted avionic instrumentation had provided remarkable results not only in identification and mapping of pigments of wall paintings, but also in the retrieval of faded traits in mural inscriptions [5]. These premises encouraged the adoption of HSI technique in the on-going research program carried out in Ostia Antica. It was expected that HSI could profitably integrate the other techniques in the identification and mapping analysis of pigments, and more generally for gaining insights into the evolution of pictorial techniques over the epochs through Ostia. The imaging modality of HSI facilitates the acquisition of analytical data covering large portions of wall surfaces, thus enabling, in principle, extensive and comparative analysis between different rooms, houses, and insulae through the site. Thus, in March 2023 a pilot HSI experimental campaign was carried out on a selection of mural paintings in two houses, in the insula of Diana and in the insula of Giove and Ganymede (Figure 4), by using an HSI compact camera of the new generation (Specim IQ), which features lightness and high optical versatility. The camera operates in the 400-1000 nm (VNIR) spectral range with 2 nm spectral resolution. This equipment can operate at variable distances from tens of cm to tens of meters, with different spatial resolutions, thus enabling, in principle, remote-sensing measurements of surfaces difficult to reach. The issues of illumination and calibration can nevertheless limit the applicability of the technique and suitable experimental set-ups had to be adopted for effective measurements. The preliminary tests indicated the capabilities of this technique not only for identifying pigments but also for mapping their distribution on the surfaces. This is particularly important for fast detection of non-original areas (previous treatments, restorations, etc.), and thus for wise choice of points in spot analysis. In addition, HSI data elaboration with multivariate analysis methods (e.g. PCA, MNF) enabled the enhancement of details that are not evident at the visual inspection (e.g. Faded decorations), thus facilitating the comparative evaluation among the different rooms, pictorial styles, etc. This first HSI campaign evidenced agreement with data acquired on the same paintings with other analytical techniques (e.g. VIL and XRF), corroborating the identification of most of the pigments more extensively used (e.g. red and yellow ochres, hematite, goethite, Egyptian blue). Moreover, the combination of reflectance spectra with XRF data provided additional information about the presence of different mixtures of pigments, despite their similar chromatic appearance.

*Figure 4. The compact HSI camera during the measurements campaign of the paintings in the main room of the Giove and Ganymede house.*

Overall, the preliminary outcomes of the HSI experimentation provided highly promising results and evidenced future perspectives of use of this methodology to reach the goals of the project.

### B. *X-Ray-Fluorescence (XRF)*

Portable XRF identifies the elemental composition of the walls and gives information on the type of pigments present. Three different portable XRF instruments were used in the study during the different campaigns in order to facilitate efficiency and also compare the overall results of different devices. To that effect, a Bruker Tracer (III/IV) and a Thermo scientific device were used simultaneously during the October 2022 campaign in order to evaluate the results of both instruments. The newly developed XRF SmART_Scan software [6] was used to convert single data points into elemental maps. These are maps showing the location of individual elements. However, the maps can also be combined visualizing those regions in which more than one element is simultaneously present. In this way compounds can be built, indicating more precisely the type of pigment present. The group testing on XRF SmART_Scan used an XRF Bruker tracer but only focused on the study of one building during the March 2023 campaign. The preliminary XRF results show that the most widespread pigments throughout all periods of Ostian wall paintings are based on earth colors such as Iron oxides, reds and yellows, umber, and green earth. However, certain more important buildings such as the Mithraeum, the House of the Seven Sages, the House of the Gardens, the Bath houses, and the House of Serapis, show the presence of Egyptian Blue (confirmed by VIL). In addition, the presence of red lead is also widespread but mostly found in higher-quality paintings and often on the clothing and shrouds of characters. Interestingly, different shades of red lead from burgundy and orange can be found, although a bright orange variety was only found on the shroud of Serapis, whereas the most common shade seen for red lead is dark red to burgundy. The presence of lead white in paintings starting during the 2nd century CE has also been observed, and in contrast with lime white which is found on earlier paintings and often mixed with Egyptian Blue, as confirmed by VIL, lead white is not, as there was no copper nor VIL image on areas with lead white. This finding is in agreement with a recent study at Villa Adriana of paintings of the same age [7]. Cinnabar was only observed on the paintings at the House of the Eagles although it has been identified in early fragments belonging to the republican era [2]. The presence of Barium in some of the sites such as the Mitraeum, suggests that the Florentine method of wall painting consolidation using Barium Carbonate was previously applied. The presence of titanium and zinc on other sites, such as the House of the charioteers, also suggests modern restorations.

### C. *Visible Induced luminescence (VIL)*

Egyptian Blue was widely found on Ostian's paintings dating from 1 BCE to 4th century CE, however, its presence appears in paintings of high status and in quantities that sensibly vary in time. Egyptian Blue is found in very large amounts in earlier periods, very often mixed with other colors, but its frequency slowly decreases in time. Budget issues and availability of the pigment, but also a change of taste and loss of technical skill in Late Antiquity might be some of the reasons why. The maps produced by SmART_scan are in agreement with those obtained by HIS and VIL, confirming the accuracy of all these techniques. Using SmART_scan combining the simultaneous presence of Ca, Cu, and Si one can simulate the EB formula and produce maps comparable to VIL.
As an example, Figure 5 shows the comparison between the SmART_scan and VIL maps on a detail of the Maenad.

### A. *External Reflectance FTIR*

Bruker alpha FTIR spectrometer with an external reflectance probe allowed for the identification of inorganic materials such as gypsum and carbonates, along with acrylic coatings. Due to the need for nearly straight surfaces for the successful use of this instrument, not all walls could successfully be analyzed by FTIR at this point, and this will be the focus of future campaigns to investigate the best set up in order to carry on the analysis and possibly also identify ancient binding media in addition to inorganics and modern coatings.

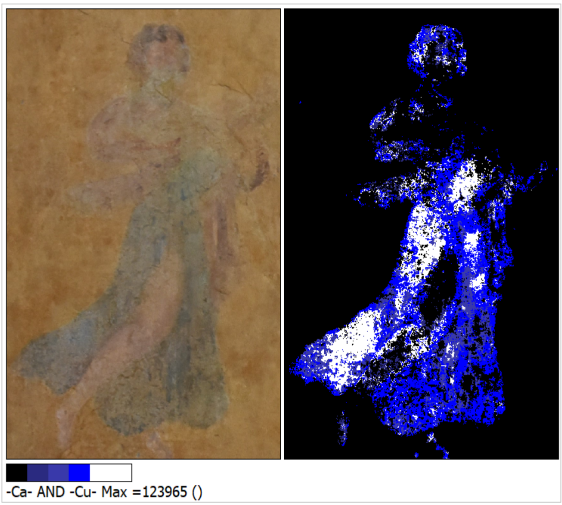


*Figure 5. a) SmART_scan map of Ca and Cu combined. b) Image obtained by VIL.*

*Table1. Noninvasive portable techniques used in the study showing the type of information obtained*

| Portable technique | Spot diam. / target size" | Application to | Information type |
|---|---|---|---|
| XRF | 1-5 mm | Pigments | Compositional info on painting materials |
| NMR depth profiling | 10 mm-40 mm Sub-surface stratigraphy up to 20 mm | Mortars, binder, organic coatings, wood | Fingerprint of mortar properties; info on manufacturing techniques; detection of covered wall paintings |
| External Reflectance FTIR | 3 mm | Organic coatings, inorganic compounds (e.g.gypsum carbonates…) | Compositional info on pictorial materials degradation products; Presence of non-original parts, restoration |
| HSI | Imaging (cm to meters) | Pigments Non-original materials, restorations, | Compositional info on pictorial materials; distribution maps Presence of non-original parts, restorations Manufacturing techniques; stylistic aspects |
| Near IR | 1 mm | Pictorial and preparation materials (e.g., gypsum, mortars) | Compositional info on pictorial materials |
| Raman | 3 mm | Pigments composition | Compositional info on pictorial materials; |
| VIL | Imaging (cm to dm) | Egyptian Blue | Detection of Egyptian Blue and distribution maps; study of its use in different stylistic epochs |
| Smart_scan/ p-XRF | Imaging 5mm (XRF) (cm to dm) | Pigments | Pigments distribution maps. Visualization of stylistic aspects |

## III. CONCLUSIONS AND FUTURE WORK

The presence of multiple research teams with varying expertise working together at one site in collaboration with archaeologists, art conservators, and restorers allows further investigation, answering both scientific and archaeological-historical questions and also aiding conservation efforts of the site. Comparison among techniques (summarized in Table 1) and routine methods along with new instrumentation and testing new devices for archaeological purposes, promises to be an important development on how a whole ancient city can be best studied in terms of its decorative art. At the same time, archaeological and art historical questions are explored.

## IV. ACKNOWLEDGMENTS

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