University of Évora

ARCHMAT
ERASMUS MUNDUS MASTER IN ARCHaeological MATerials Science

Revitalising a historic knowledge resource: an archaeometric investigation of the Mora wall painting Sample Collection (ICCROM)

Cecilia Laurita

Prof. Dr. António José Estevão Grande Candeias, Universidade de Évora, Supervisor

Doctor Milene Gil Duarte Casal, Universidade de Évora, Supervisor

Doctor Alison Heritage, ICCROM, Co-Supervisor

Évora, Portugal, October 2018

University of Évora

ARCHMAT
ERASMUS MUNDUS MASTER IN ARCHaeological MATerials Science

Revitalising a historic knowledge resource: an archaeometric investigation of the Mora wall painting Sample Collection (ICCROM)

Cecilia Laurita

Prof. Dr. António José Estevão Grande Candeias, Universidade de Évora, Supervisor

Doctor Milene Gil Duarte Casal, Universidade de Évora, Supervisor

Doctor Alison Heritage, ICCROM, Co-Supervisor

Évora, Portugal, October 2018

Acknowledgements

The development of this thesis has been a really challenging, dense and stimulating work and I here sincerely wish to thank all the people who directly or indirectly contributed to it.

First of all, I would like to express my gratitude to my supervisors Professor Antonio Candeias and Doctor Milene Gil for their continuous precious support. I feel privileged for the great chance and opportunity they gave me to work in one of the worldwide most important and renowned centre for the conservation of cultural heritage. I here want to thank also my co-supervisor Doctor Alison Heritage and Doctor Maria Mata Caravaca for being my guides and referees during my research period at ICCROM. It has been an honour and a pleasure to work in such a rich ambient in terms of knowledge and beautiful people. In this respect, I would like to thank Annalaura and Gabriele, my lifesavers during the long days in the laboratory.

My thanks go also to Doctor Giovanna Meloni, from the ISCR, who helped me with patience and understanding during the complicated research in the archives.

I would like to thank Sara Valadas, Ana Cardoso, Mafalda Dias and Miriam Pressato from HERCULES laboratory of the University of Évora for having represented an essential part in this work, carrying out the analysis that I could not conduct for logistics reasons and for always being available for help and explanations. I would also like to thank the people that I met in HERCULES during the last years and that influenced and enriched my life.

I would like to express my acknowledgments to all the ARCHMAT consortium and to Fundação para a Ciência e Tecnologia - FCT for their financial support through

PTDC/EPH-PAT/4684/2014 project: DB-Heritage - Heriage database on historical construction materials.

Thanks to all my ARCHMAT fellows, because the world is not so big as it seems.

A special thank is evidently due to my friends Silvia, Francesca and Silvia, because people who deserve gratitude, they know it.

Thanks to Valerio, because being far is not easy, but feeling close is even harder.

My greatest and last thanks are for my sisters and my parents for their endless support and love, because I would not be here, in this hard and beautiful moment of my life, if it were not for them.

Panel of Jury

President: Professor Nicola Schiavon, Universidade de Évora;

Examiner: Professor Patrícia Sofia Martins Moita, Universidade de Évora;

Supervisor: Doctor Milene Gil Duarte Casal, Laboratorio HERCULES, Évora;

Partner member: Professor Mary Anne Tafuri, Universitá di Roma La Sapienza.

Abstract

Revitalising a historic knowledge resource: an archeometric investigation of the Mora wall painting sample collection (ICCROM).

This master's thesis focuses on the archaeometric investigation of the Mora wall painting Sample Collection, held at the International Centre for the Study of the Preservation and Restoration of Cultural Property (ICCROM), in Rome, Italy.

The collection itself is considered as a unique resource for understanding ancient wall painting technologies. The overall aim of this study was to explore its potential value through the analytical investigation of samples and through the research of contextual information within the ICCROM's Archives.

The selected multi-analytical methodology consisted mainly of portable instrumentation (optical digital microscopes, spectrophotometer, FORS, h-XRF) and micro-invasive techniques (micro-FTIR and micro-XRD).

According to the acquired data, the chromatic palette of the analysed fragments consisted of red and yellow ochres, cinnabar, minium, green earth and Egyptian blue; the binding material revealed was calcite. The painting technique could be either fresco or a secco lime-painting, since stratigraphic information of the samples were lacking.

Resumo

Revitalizar uma fonte de conhecimento histórico: investigação arqueométrica da coleção de amostras de pinturas murais dos Mora (ICCROM).

O presente trabalho é dedicado á investigação arqueométrica dos fragmentos de pintura mural da Colecção Mora, conduzidas no Centro Internacional para o Estudo da Preservação e Restauração de Propriedade Cultural (ICCROM), em Roma, Itália.

A colecção de Paolo e Laura Mora é considerada única no âmbito de compreender as tecnologias utilizadas na execução de pinturas murais antigas.

O objectivo principal desta investigação foi de explorar o potencial valor da colecção através da investigação analítica de amostras, em conjunto com a pesquisa de informação contextual presente no arquivo do ICCROM.

A metodologia multi-analítica selecionada para este trabalho consiste essencialmente no emprego de instrumentações portáteis (microscopia óptica, colorimetria, FORS e h-XRF) e técnicas micro-invasivas (μ-FTIR e μ-XRD).

De acordo com os resultados obtidos, nas camadas de pintura investigadas estavam presentes vermelho ocre e amarelo ocre, cinábrio, minium, verde terra e azul egípcio. O material ligante foi identificado como calcita e nenhum material orgânico foi detectado. A técnica de pintura mural utilizada pode ter sido tanto *a fresco* como pintura a cal *a secco*.

Contents

List of Figures

List of Tables

Chapter 1

Introduction

1.1 Object of Study

This master's thesis focuses on the archaeometric investigation of the mural painting sample collection held at the International Centre for the Study of the Preservation and Restoration of Cultural Property (ICCROM) in Rome, Italy.

ICCROM was founded in 1959 as a centre for promoting the conservation of all forms of cultural heritage, including the mural paintings. In particular, it holds one of the most valuable wall painting sample collection, which is the main subject of this study. The collection comprises more than 1400 material samples donated by two internationally renowned conservator-restorers Paolo and Laura Mora. Among other commitments, they were involved in the coordination of ICCROM's Mural Painting Conservation courses. The Paolo and Laura Mora Mural Painting Sample Collection (hereafter the Mora Sample Collection) was assembled in order to study the different mural painting techniques and materials used by different cultures and civilizations. The Moras collected the samples from heritage sites throughout the world, during numerous technical missions and conservation campaigns during approximately twenty years, from the 1960s to the 1980s[1]. Almost 300 fragments of wall paintings within the collection come from sites around Rome and Naples. The representative nature of these sample collection could allow a new insights into the Roman wall painting technology.

---

[1] https://www.iccrom.org/news/request-proposal-mora-sample-collection

The large amount of unstudied material samples within the Mora collection is a unique resource for further investigation of those heritage sites and future conservation research. Nevertheless, documentation about the collection diagnostic scientific studies are largely absent.

The present master research is part of the on-going project "Documentation, reorganisation and study of the ICCROM Mora Sample Collection", led by the HERCULES Laboratory of the University of Évora (Portugal) [2] , which hopes to rectify this gap in knowledge. The mentioned project has 3 main goals. Firstly, the identification, description and characterisation of the fragments. Second, to safeguard the collection, through the re-organisation and re-housing of the fragments. Third, the promotion and dissemination of the results of this project, through the creation of an on-line catalogue, available on the ICCROM's website[3].

1.2 Scope and research questions

The overall aim of the current research is to explore the potential value of the Mora sample archive as a resource for the study of ancient wall painting technologies. In order to achieve this, 4 research questions were formulated:

1. How many samples were already analysed and with which analytical techniques and what were the main conclusions about technical and material features?
2. How can the scientific data be organized in a work sheet for on-line dissemination and future academic research?
3. Which are the advantages and limitations of the combined use of portable and non-invasive instrumentation for *in situ* characterisation of pigments and binders?
4. Which are the main pigments in the Roman period collection and which was the most frequently used painting technique (*fresco* or *a secco*)?

---

[2] HERCULES (HERança CULtural, Estudos e Salvaguarda) Laboratory, http://hercules.uevora.pt/

[3] Proposal-Mora Sample Collection-Lab HERCULES-December 2017

Taking these inquiries into account, 4 main objectives were defined. The first objective was to document the Mora samples archive through the systematic collection of characteristic data concerning the fragments that it comprises, in particular technical and material features.

The second objective was the establishment of a methodology for organizing the collected data into a structured catalogue proforma.

The third objective was the establishment of a methodology for the *in situ*, non-invasive characterisation of painting materials (pigments and binders).

Finally, to increase the existing body of knowledge concerning the technology of Roman wall paintings through the analytical study of mural painting samples.

This master thesis has been compiled within the Erasmus Mundus master's program in Archaeological Materials Science (ARCHMAT). The research was carried out from January to July 2018 in the scientific laboratory and archives of ICCROM under the supervision of Dr. Milene Gil from HERCULES Laboratory.

1.3 Thesis structure

The present research has been organized into five chapters.

The first chapter provides the reader with an introduction to the subject material, as well as its position in the context of a larger project on the cataloguing and reorganisation of the same materials. The main objectives and research aims behind this study are elaborated and the thesis structure is further described.

The second chapter includes a background of this study, providing a description of ICCROM, where the mural paintings collection is located. This chapter presents Paolo and Laura Mora and their role in assembling the Mora Sample Collection. In addition, the main features and techniques of mural paintings are reported.

The third chapter focuses on the Roman wall paintings, the main case study of this thesis. The state of the art on materials and techniques of the Roman mural paintings is discussed. Following, the samples are described in detail. The methodology and the experimental conditions used for carrying out the analyses both *in situ* and in the laboratory are presented.

In the fourth chapter, the results obtained through the experimental work are reported and discussed. The technical and material data of the fragments analysed are displayed, divided in two main sections: pigments and binders. Moreover, the advantages and limitations of the used analytical techniques are considered and deliberated.

The fifth and last chapter reports the conclusions of the work and some final thoughts, as well as proposals for the continuation of this study.

Chapter 2

ICCROM Mission and the Mora Sample Collection

2.1 ICCROM definition and mission

ICCROM is an intergovernmental organisation that operates to promote the conservation of cultural heritage world-wide. ICCROM's headquarters is located in Rome, Italy, and it supports 135 Member States in safeguarding all forms of heritage within their borders and beyond. It collaborates with institutions and professionals at an international and governmental level, relying mainly on formal collaborations with organisations such as UNESCO [1], ICOMOS [2], ICOM [3], ICA [4] and IIC [5]. [6]

The Centre was founded in Rome in 1959 in the aftermath of the Second World War. In order to face the widespread destruction and the urgent need for reconstruction, a proposal was adopted during the 1956 UNESCO General Conference in New Delhi to establish a centre for the study of matters related to the conservation and protection of cultural heritage. [7]

Since the early 1960s, the Centre has been organising training activities, work-

---

[1] United Nations Educational, Scientific and Cultural Organization

[2] International Council on Monuments and Sites

[3] International Council of Museums

[4] International Council on Archives

[5] International Institute for Conservation

[6] https://www.iccrom.org/about/overview/what-iccrom

[7] https://whc.unesco.org/en/partners/284

shops and courses for conservators around the world. Dr Harold J. Plenderleith was the first director of ICCROM, until 1971. Previous to this, he was the keeper of the Research Laboratory at the British Museum in London and in 1966 he set up a laboratory at the Centre. Throughout the years the laboratory was moved and expanded and new equipment was installed to support the very popular conservation courses that ICCROM ran at that time. Starting in 1968, the annual course on the conservation of mural paintings was one of the most popular activities. It was coordinated jointly with the Istituto Centrale del Restauro (ICR, Central Institute for Restoration) in Rome, today called ISCR- Istituto Superiore per la Conservazione ed il Restauro (Superior Institute for the Conservation and Restoration) [8].

An international library and documentation centre was also established at ICCROM, and is today one of the most important resources for conservators in the world. The ICCROM archive represents an essential resource for research and study as well as holding institutional records in the form of papers, photographs, video and audio from the creation of the Centre to the present.

Over the years, ICCROM participated in several international missions and campaigns for conserving and restoring all forms of cultural heritage. It promotes an interdisciplinary approach to conservation involving scientists, conservators, restorers, art historians, archaeologists, architects and engineers, among other professionals[9].

It is in the ICCROM library and archive that the research and documentation for the present thesis was carried out, whereas the scientific investigation and analysis of the materials was conducted within the ICCROM laboratory.

2.2 Paolo and Laura Mora: an overview

Paolo Mora and his wife Laura Sbordoni (shown in Figure 2.1) were chief restorers and conservators at the Istituto Centrale per il Restauro (ICR), the main Italian institute for conservation practice. They were also consultants and collaborators of ICCROM. Their team also comprised the art historian and critic Giovanni Urbani

---

[8] https://www.iccrom.org/about/overview/history

[9] https://www.iccrom.org

Figure 2.1: Laura and Paolo Mora, Venezia, 1967. ©ICCROM

and the theorist Cesare Brandi, who founded the ICR in 1939, together with the critic Giulio Carlo Argan. Together, they played an essential role as researchers and teachers, establishing modern conservation practice and promoting the excellence of Italian restoration throughout the world.[10]

Paolo and Laura Mora undertook numerous projects and missions for conserving and restoring paintings around the world. They were famous for their cleaning abilities and consolidation techniques, as well as their method of facing the problem of image restoration and presentation. Over the years they carried out missions in approximately 36 countries. Their last project was managing one of the most complex and challenging conservation problems: the consolidation and restoration of the mural paintings in the Egyptian tomb of Queen Nefertari.[11]

The Moras were also involved in several training and teaching activities, playing an educational role, not only for Italians at the ICR but also for international students through the ICCROM courses. They were lecturers at the ICCROM's annual Mural Painting Course, to which they contributed on the design and implementation.

With such a wealth of experience Paolo and Laura Mora decided to document

---

[10] http://www.treccani.it/enciclopedia/paolo-emilio-mora

[11] https://www.iccrom.org/news/laura-mora-1923-2015

and communicate their methods to a wider public by writing and publishing The Conservation of Wall Paintings, a complete treatise on the techniques and conservation of mural paintings. With the ICCROM Director Paul Philippot as co-author, their intent was to create a didactic manual to face the problems with a general methodology, highlighting the importance of interdisciplinary work [26].

2.3 The Mora Sample Collection

During their several missions and conservation campaigns, Paolo and Laura Mora collected numerous material samples from different heritage sites around the world. Their aim was to investigate and analyse the variety of wall painting techniques used by different cultures throughout time. They selected these materials presumably in order to study and use them during the practical classes of the ICCROM courses, especially the Mural Painting Conservation one. After their retirement, the Moras donated these materials to the Centre that assembled and stored them into a unique collection. [12]

According to the ICCROM catalogue, the Mora Sample Collection is composed of more than 1400 material samples, including fragments of wall paintings and ceramics, as well as prepared thin sections and cross sections. The Collection holds samples from monuments belonging to 35 different countries such as Algeria, Egypt, Greece, Iran, Italy, Turkey, Israel (as shown in Table A.1 in Appendix A).

Sometimes admirers and followers of the Moras donated them materials otherwise unobtainable, in order for them to increase their knowledge on wall paintings. This kind of donations is documented through some handwritten notes that were found within the collection during this research work.

The relevance of the Mora Sample Collection is also highlighted by the fact that in many of the heritage sites represented in the collection, sampling is nowadays forbidden. Therefore, the collected materials are a very important resource which, together with contextual information, could allow further investigations of these sites.

---

[12] https://www.iccrom.org/news/request-proposal-mora-sample-collection

Despite its potential, the collection had been neglected for a long period of time. The samples lack a proper description, label and adequate storage measures for long-term conservation. In order to protect the collection, ICCROM opened a call for a project in June 2017 to document, catalogue, re-organise and re-house the Mora Sample Collection [13]. The project was then granted to Dr. Milene Gil from HERCULES Laboratory of the University of Évora, and it is within this project that the current thesis research took place.

2.4 Previous analytical studies

Since the wall painting materials within the collection were most likely collected by the Moras and their colleagues for a didactic purpose, previous scientific studies were expected on fragments, as well as on already prepared thin and cross sections. Together with these materials, glass holders containing powdered pigments and plasters, most likely collected for analysis, are also part of the collection.

The first goal of this project, was to gather information about the previous studies conducted on the collection, to understand how many of the materials had already been analysed, and with which analytical techniques. This will aid future researchers in building upon previously acquired knowledge and proposing more productive research designs. In particular, this thesis focuses on the analysis of Roman samples in the collection. Since the fourth objective is to characterise the paint layers, the compilation of analyses on these materials was paramount and necessary. Special attention was paid to the samples from the Roman period. However, no information on the Roman samples was obtained in the research conducted on ICCROM's archive, and therefore it was assumed that no major previous analysis had been done.

Other samples from Afghanistan, Algeria, Egypt, Greece, Peru and some Italian cities (Assisi, Novara, Orvieto, Tarquinia) in the collection were found within the archive's mission reports. Information about samples coming from Egypt were assembled in 1996 through a documentation project about a conservation campaign in

---

[13] https://www.iccrom.org/news/request-proposal-mora-sample-collection

Figure 2.2: Laura and Paolo Mora, Valley Nobles, Egypt, 1970. ©ICCROM

the Nile Valley in the 1960s [14] (Figure 2.2). Therefore, the information about these samples is far more detailed. The documentation includes technical and mission reports, letters, photos and a collection of slides showing samples in cross section. The analytical studies mentioned in the documents refers to analysis carried out by the ICR (today ISCR) scientific laboratories, including analyses in thin section and via X-Rays Diffraction of the plasters and paint layers.

Thus, in order to obtain more information about previous studies, further investigations were carried out at the ISCR archive and library. The archive contains a myriad of information, concerning analyses done during the Moras' lifetime, but the cataloguing system used is very cryptic. The consultation was not straightforward and no data related to the samples was found. Therefore, it is possible that information about other samples from the Mora Sample Collection exist in the ISCR archive,

---

[14] "The Safeguard of the Nile Valley Monuments, as seen through ICCROM's Archives" CD-ROM ©1996 ICCROM

but for this study they could not be accessed. Future research at the ISCR archive is needed for a more detailed picture of the entire Mora Sample Collection.

2.5 Mural paintings

In this section, a short description on the main aspects of the structure and techniques of mural paintings is presented.

2.5.1 Support

The term "support" is used to define the surface on which the painting is executed and it refers to a wall, which can be natural or artificial. The painting can be executed either directly on the support or on a previously applied layer called rendering or ground, usually consisting of a lime-based plaster and aggregates. The rendering is often composed of two layers called *arriccio* and *intonaco*. *Arriccio* is a rough sub-layer applied to even out the surface of the wall and sometimes to keep it damp, as in the case of *fresco*. *Intonaco* is the thin and smooth layer that receives the painting. In some cases, the *intonaco* can be covered or replaced by a thin layer of lime-wash called "whitewash", in order to achieve a brighter background for the painting [26].

2.5.2 Binding media

Binders or binding media are the components of a painting that are responsible for the reciprocal joining of the pigment particles and their attachment on the support in the form of a thin layer [4]. These materials should be immutable through time, in both their chemical and photochemical properties, so as to avoid changing the aesthetic of the painting [4]. Binders can be very useful elements to identify painting techniques [4, 19].

2.5.3 *A fresco* techniques

The term *fresco* or *affresco* is used for paintings executed by applying pigments on fresh plaster while still damp. In this way, the pigments are fixed on the surface by the carbonisation of the lime (calcium hydroxide) contained in the plaster layer (*intonaco* or whitewash) [1]. The *intonaco* is applied onto the portion of the *arriccio* that can be painted in one day, called *giornata*, which means one day's work [15]. The pigment is mixed with water and applied on the rendering surface. As the base starts to dry, the saturated calcium hydroxide solution ($Ca(OH)_2$) migrates towards the surface and reacts with the carbon dioxide (CO_2) in the air. The final product is calcium carbonate (CO_3) and water that evaporates [26]:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \tag{2.1}$$

During this reaction the pigments get fixed by the crystallisation of the carbonates on the surface and become an integral part of the support [26].

The application of pigments on damp plaster mixed only with water is called Buon *fresco* (pure *fresco*). It was described for the first time in the 15th century by the Italian painter Cennino Cennini, in his book Il Libro dell'arte, a treatise on Medieval and Renaissance painting [8]. In this technique the use of a binder is not necessary since the pigments are secured through the carbonisation of lime. The final effect resembles water colour painting do to its translucent quality[26].

Sometimes the pigments can be mixed with lime water or milk of lime, instead of pure water: in this case the technique is called Lime *fresco*.

In other cases, a medium can also be added to the pigments as a "supplementary element", in order to achieve a particular texture or gloss effect or because of the characteristic nature of certain pigments [26]. This technique is still called *fresco*, even with the addition of a tempera medium, such as casein. The reason for this nomenclature is the continue reliance on the carbonisation of lime reaction to fix the pigments and the application of these on fresh plaster [26].

2.5.4 *A secco* techniques

The term *a secco* is used for those forms of painting where the pigments are applied directly on a dry plaster or dry whitewash. In the *a secco* techniques the pigments need to be mixed with a binder before their application to ensure adherence to the support.

The first type of *a secco* technique is called "lime painting". Here, the pictorial layer is fixed to the support by means of a lime or milk of lime binder that is included in the paint mixture [26].

Two other common types of *a secco* techniques employed rely on tempera and oil as binding mediums paintings with tempera and oil. In *tempera* paintings, pigments are mixed with a medium that fixes them as they dry. The most prevalent binders used in the tempera technique are of protein origin, such as casein, egg, animal glue or vegetable gums. They can be used either as aqueous solutions or in emulsion. Oil paintings commonly use linseed oil or poppy-seed oil as binders[26].

Chapter 3

Case study

3.1 State of the art

In the mid-1960s, Paolo and Laura Mora, together with the ICCROM Director Paul Philippot, formulated a theory regarding the technique used in Roman wall paintings that guided preservation and restoration works around the globe for decades: the so-called "*fresco* theory", or "Mora-Philippot theory of *fresco*". They postulated that the standard technique used in Roman wall paintings was *a fresco* [26]. In their book "Conservation of Wall Paintings" , the authors follow the development of *fresco* during the different Styles of Roman wall painting assuming that this was the technique used for all murals during all Roman time periods [6, 15, 26].

The Moras and Philippot based their theory on both inspections of the characteristics of different Roman mural paintings and on literary references such as Book VII of the "De Architectura" by Vitruvius [37], and Pliny's "Historis Naturalis" [26]. Vitruvius' book in particular serves as basis to their entire theoretical framework. The authors did a close reading of the primary sources and analysed the meaning words that could be controversial in terms of painting techniques. Pliny's text was used as a confirmation, being it a second, independent voice, dating at least a century after Vitruvius [37].

The technique was described by Vitruvius and summarised by the Moras-Philippot [26] as:

- first, several rough layers of lime and sand are applied, with the aid of square and plumb line, in order to even out the wall; this approximately corresponds to the *arriccio* typical of works from the Renaissance;

- a second, finer layer, with a mortar made of marble powder, is applied and well smoothed by rubbing the surface; the marble powder allows to enhance this smooth effect, and the instrumental action gives an overall compactness and solidity to the surface;
- the final stage, crucial for the distinction of *fresco* from secco techniques, is the application of colours and the following *politiones* to which the whole illustrated portion of the wall is subjected. In *frescoes*, as already mentioned in the previous chapter, the pigments are diluted in simple water and directly applied on the fresh plaster while it is still damp. The carbonisation of the lime contained in the plaster layer fixes the pigments to the surface and guarantees their permanence.

According to the Moras and Philippot, these *politiones* cited by Vitruvius [37] are nothing else than polishes, supposedly made with sturdy tools, that take advantage of the presence of marble powder in the plaster. The hypothesis about the tools is advanced by the authors as a justification to the observable markings left on the paintings. Since the previous hypothesis of polishes via abrasion would contradict the greasy, unctuous appearance of the mural.

To preserve the dampness of the plaster long enough for the painter (or painters) to complete their creations, *frescos* would have been realized in a discontinuous manner. Each day the *intonaco* was applied over the rougher *arriccio* only in the portion of wall that could realistically be painted. This would constitute the setting for the daily work, and was called *giornata*. The plastering was carefully applied so as to hide every trace of a joint. Since the innermost layers of mortar would remain somewhat damp for more than just one day, the polishing phase would finally adjoin *giornate* together. Another cited technique prescribes to align the boundaries of each *giornata* to contour lines of the painting, as to make their *joints* less perceptible [26].

Several *giornate* would be necessary to complete one *pontata*, which is the name used for the portion of mural painting to be performed before the need to move the scaffolding. The Moras and Philippot defend their theory against objections regarding the time it would have took to complete the most complex murals: painters would still be able, at the end of the day, to cut out any unwanted or incomplete sections of the *giornata*, to carry on in the following days [26].

The "*fresco* theory" discards, in general, the idea that Roman mural paintings would have commonly been realized with *a secco* techniques, which require pigments to be applied with a binder, usually of organic nature. The authors even dismiss the possibility that backgrounds were *frescoes* while figures and detailed motifs were *a secco*, citing once again Vitruvius indicating that his work completely lacks a section devoted to the necessary mediums.

After its formulation, the "*fresco* theory" quickly became *the* theory according to which all preservation and restoration works on Roman wall paintings were performed. The Moras developed specific conservation treatments basing them on this identification of the painting technique [1]. With ICCROM's international audience and scientifically re-known laboratories, the "*fresco* theory" was quickly accepted by other institutions responsible for the conservation of Roman murals, ignoring other existing theories which were developed contemporaneously.

Two main repercussions occurred due to this phenomenon. The first is that conservation treatments can be very technique-specific, to the point of harming paintings that weren't properly identified. For example, treatments suggested and applied by the Moras included the dissolution of any trace of beeswax by means of organic solvents [26]. This is not harmful for *frescos*, since the binding action is through lime, but it can be a problem for murals where beeswax is a component of the binder. The "*fresco* theory" explains the presence of beeswax as the remainder of prior conservation treatments, and thus, implies and even encourages the applicability of the aforementioned solvents [2].

---

[1] Mora L, Mora P, Torraca G, Bonito VA. A coordinated methodology for the treatment and study of the peristyle garden wall of the House of Menander, Pompeii: an interim report. In: Case studies in the conservation of stone and wall paintings. Bologna: Contributions to the 1986 IIC Congress; 1986. p. 39.

[2] Mora L, Mora P, Torraca G, Bonito VA. A coordinated methodology for the treatment and study of the peristyle garden wall of the House of Menander, Pompeii: an interim report. In: Case studies in the conservation of stone and wall paintings. Bologna: Contributions to the 1986 IIC

Second, nowadays through scientific analyses researchers have debunked many of main precepts of the *fresco* theory raising doubts of its widespread applicability. Current research suggests that several Roman wall paintings were performed using *secco* techniques [2, 11, 35]. In light of the extreme specificity of some conservation treatments, the problem of definitively identifying the painting technique becomes paramount. Since new research has caused disagreements about the general nature of ancient paintings, the appropriate conservation treatments must be made specific to the painting [15].

A very precise and thorough review of ”confounding factors in ancient paint media analysis” has been carried out by Jorge Cuní in 2016 [15]. His arguments and criticisms are used as a guide to present the current debates in conservation practices.

Cuní argues that the *fresco* theory as formulated by Paolo and Laura Mora and Paul Philippot is outdates due to the following points.

Different painting techniques on wet supports

The Moras and Philippot base their theory on the fact that distinctive marks and depressions in coloured plaster backgrounds imply that they were painted onto a fresh rendering. They cite Vitruvius' statement that only colours applied on a wet support are permanent, suggesting that the artists used to paint on fresh lime layers. While this is generally agreed upon, Cuní argues that the main assumption of the *fresco* theory, which is that this technique only corresponds to *fresco* painting, is incomplete at best. It disregards completely the (documented) existence of other painting techniques that become water resistant when applied on damp renderings. Such is the case, for example, of emulsified wax paint, whose ”soap content reacts with the lime, quickly transforming it into an insoluble calcium soap, and making the paint water-resistant” [3] [15].

Components of emulsified wax paint have in fact been identified in several Roman wall paintings, and references to the use of beeswax paint are not uncommon in

---

Congress. IIC; 1986. p. 40.

[3] Cuni J. What do we know of Roman wall painting technique? Potential confounding factors in ancient paint media analysis. *HeritSci* 2016. p.6

ancient texts [4] [5] [6] [7].

Long *pontate*

Cuní argues that principle that artists are only able to paint one *pontata* a day (excluding the more complex parts), is not realistic. The Moras and Philippot explicitly describe a "typical working surface without joints", "around 2 m high by 5-6 m long"[8]. Cuní cites an experimental study carried out by Alix Barbet [9], that produced a minimum of three joints while painting a very similar 2.20 m per 4.48 m surface, all while employing a team of eight painters. Some areas even remained unfinished [10].

Giornate (or the lack of them)

The most complex parts of each *pontata*, that the Moras and Philippot identify as "capitals, pilasters and panels of imitation marble" and as a number of "inserted pictures", were supposedly painted in a separate moment, meaning in a distinct *giornate*. The author cites an experimental study by Shigeru Tsuji on wall paintings in the Room of Elephants in the House of the Lararium of Achilles in Pompeii [11]. Tsuji, after a thorough examination, concludes that no *giornate* joints can be identified, even though Mora and Philippot used this particular room as an example of their theory. Cuní also argues that the insertion of figures onto finished wall paintings, and the joints that necessarily ensue, are not exclusives of *fresco* techniques. This underlines the peculiarity of such discreet joints mentioned by the Moras, especially when confronted with the much more conspicuous joints of Renaissance *frescoes*.

---

[4] Erechtheion inscription IG 13 476.25, Expenses 7/408-6/407 BC.

[5] Hill BH. Structural notes on the Erechtheum. Am J Archaeol.1910;14(3):292.

[6] Laurie AP. Greek and Roman methods of painting. Cambridge: Cambridge University Press; 1910. p.56.

[7] Sarsfield WB. A Manual of Fresco and Encaustic Painting. London: Chapman and Hall; 1843. p. 19.

[8] Mora P. Proposte sulla tecnica della pittura murale romana. Bollettino ICR. 1967. p. 69.

[9] Alix Barbet, La peinture murale romaine (les styles decoratifs pompeiens), Paris, Picard, 1985

[10] Barbet A, Coutelas A. Une fresque Ã la romaine. Archéologia.2002;392:25.

[11] Tsuji S. The origin of *Buon fresco*. Zeitschrift für Kunstgeschichte.1983;46(2):216

Unaccounted alkali-sensitive pigments and white pigments

The theory of *fresco* did not account for the presence in Roman wall paintings of alkali-sensitive pigments, as recounted by several researches [10, 15, 19]. These colours, such as organic pigments, white and red lead, malachite, or azurite, cannot be used in *fresco* since they are sensitive to fresh lime. Moreover, Vitruvius himself cites malachite, purple and Armenian blue (a mix of purple and azurite) as commonly used colours to cover entire walls [37].

Other doubts arise from the lack of references in Vitruvius' and Pliny's works to lime and lime white as white pigments. Despite the fact that both cite the known white pigments, and that lime and lime white are the most common white pigments for *fresco* painting.

An unnamed technique?

Cuní briefly cites the curious fact that no special name exists to designate the *fresco* technique in either Roman or Greek language, despite it being, at least according to the *fresco* theory, common practice. One of the possible explanations for this, among the many, is that *fresco* painting technique did not exist at all in Greek and Roman times.

It would be easy, considering all these facts, to dismiss the *fresco* theory altogether, and to deduce instead that Roman wall paintings had to have been made using organic binders.

However objections can be raised to the results of research that has tried to identify binder components. Some curious facts surrounding these researches have also been presented by Cuní in the same paper [15].

The first one, regarding the distribution of binders found as a function of time and space (when and where the wall painting was realized) and research team (who was carrying out the analysis). Although one may expect the use of different painting techniques and binders in Roman murals thorough history, results of studies [2, 11, 19, 35] have proven "rather homogeneous" even when investigating binders in samples dating from centuries and continents apart. The homogeneity lies in the research team only. As the author reports, each research team usually finds a different kind of binder, but in all samples [15].

The consequences of this curious fact have propelled this thesis research since the techniques used to extract binder components may be insufficiently precise. Techniques that only use a very small amount of binder, such as FTIR or GC-MS, may be improper to conclude the absence of binder and that the painting was therefore realized *a fresco.*

The usual presence of microorganisms in ancient wall paintings can also be a source of confusion, since "it can provide an additional source of organic material that could be mistaken as part of the original binder"[12] [15].

One may conclude that further research is needed in the analysis of ancient paint media, in order to rid ourselves of the uncertainties surrounding ancient painting techniques, especially those used in Roman murals. This necessity is exacerbated by the dependency of proper conservation and restoration techniques based on specific painting techniques. Until a standardized protocol can be reached, particular care should be exercised when working on these samples.

3.2 Samples

The Mora Sample Collection contains almost three hundred mural painting fragments which had been collected among Rome, Pompeii and Herculaneum, as indicated by the labels attached on the samples containers. Unfortunately, precise references of the sites of provenance were lacking, as well as any clear indication of their time period. The old catalogue of the collection and the documentation found in the ICCROM archive about the Moras' missions were not enough to attribute an exact age and provenance to the fragments coming from Lazio and Campania regions. However, due to their stylistic aspects, as well as their chromatic palette and some descriptive labels linked to them, most of the fragments were attributed to the Roman period, without being able to discriminate the exact period.

---

[12] Cuni J. What do we know of Roman wall painting technique? Potential confounding factors in ancient paint media analysis. *HeritSci* 2016. p.4

Such a rich collection forced us to conceive this study as a preliminary research, and to select an amount of samples compatible with time availability. Therefore, a selection of 56 fragments was taken into account for analytical studies, aimed at characterising the pigments and the binders of the paint layers using the portable and non-invasive analytical setup.

Together with fragments coming from Rome and Pompeii, in the selection are included: two fragments from the Etruscan necropolis Tarquinia, one of them collected from the "Tomb of the Bulls", dated around the 6th century BC; four fragments from Viterbo (Lazio region), one of them collected from the Cappella Mazzatosta (Renaissance); three fragments from a temple in Velia (Campania region), dated around the 5th century BC; two samples from Egypt (a mural painting fragment and a little blue ball). These last fragments were selected in order to obtain a broader range of data concerning the used pigments.

All of the 56 samples were studied *in situ*, within ICCROM's laboratory, using HERCULES' equipment. Among these fragments, a subset of 15 was selected for micro-sampling, in order to further characterise pigments and binders by means of micro-FTIR. These material samples were coming from Rome (area of Palatino) and Pompeii and were presenting some characteristics typical of *a secco* techniques, as reported in the diagram of Figure 3.1. In particular, this additional selection followed some criteria and included:

- fragments with a blue or green paint layer, since these pigments were historically the most likely used with *a secco* painting technique;
- fragments presenting colours uncommon to a *fresco* chromatic palette;
- fragments presenting overlapping paint layers or characterised by a glossy surface appearance, which can indicate the use of *a secco* technique.

The table reported in Appendix B contains information about the fragments' provenance, a description of their paint layers visual colour and the temporary reference assigned to them and used during this study; the selected subset of 15 fragments is highlighted.

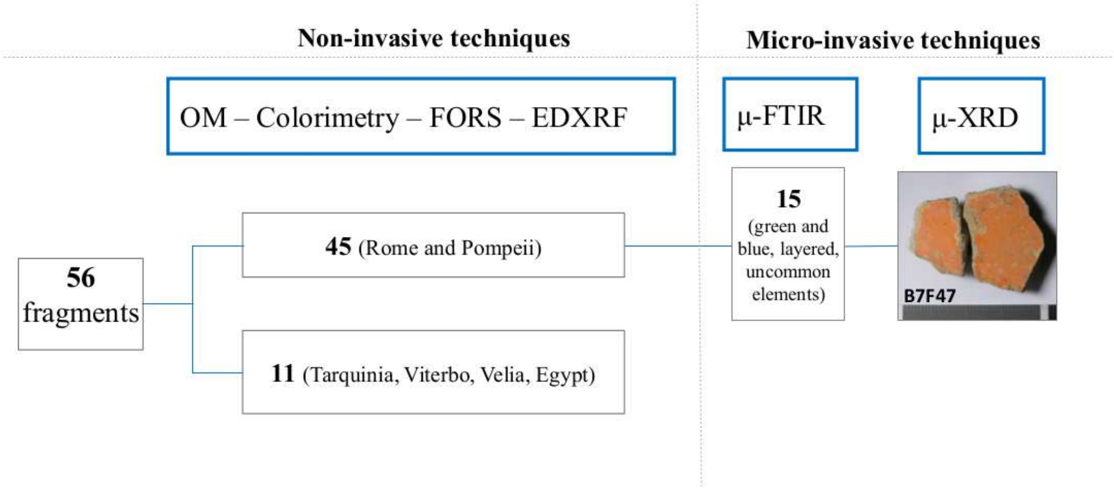


Figure 3.1: Diagram of materials and methods.

3.3 Methodology and experimental conditions

3.3.1 *In situ* non-invasive analyses

The identification of pigments in mural paintings and the determination of the execution techniques are very important for art historians and conservators to select suitable conservation procedures and correctly define restoration plans [13]. In many cases, when sampling is not permitted, the non-invasive techniques are the only applicable diagnostic tool. In studying mural paintings, the non-invasive techniques present several advantages, such as rapidity, absence of sample preparation, repeatability and portability, very important for travelling professionals who must bring the equipment to the site [13]. One of the main disadvantages of the non-invasive procedures is that, in most cases, they are not exhaustive, since they collect data which represent the constituents detected at the point of measurement or at the surface. Consequently, in order to obtain an exhaustive materials characterisation, a multi-analytical methodology is required [18].

Portable Optical Microscopy

The first stage of *in situ* analysis consisted of visual and optical observations of the mural painting fragments. Portable optical digital microscopes were used in order to obtain a first overview on the materials, painting techniques, details and a preliminary pigment characterisation.

These instruments have capabilities and advantages of traditional optical microscopes, adding ease of transport and easy handling, two important features for *in situ* analysis, especially in mural paintings. They generally use reflected visible and UV light and they can offer magnifications between 10x and 1000x, depending on the objective of the investigation. The image created by this equipment can simultaneously be viewed on the computer screen and recorded as a digital image.

Experimental conditions - The optical imaging for this study was acquired through two types of handheld digital microscopes (Dino-Lite, AR Naarden, The Netherlands): Dino-Lite Premier AD3713 TB and Dino-Lite PRO AM413T-FVW working in the reflected visible light at 20x, 50x, 60x and 435x magnifications.

Spectro-colorimetry

Spectrophotometers are optical instruments that measure the relative quantity of electromagnetic power reflected or transmitted at individual wavelengths of the spectrum [23]. The spectrophotometric curves can be plotted when a material reflects or transmits a certain quantity of light across a particular region of the spectrum. These curves show reflection or transmission as a function of wavelength and they usually present a specific shape, characteristic of the chemical properties of the materials [23].

As a matter of fact, the colour objectivity is a key factor in the art study and conservation. Since the colour evaluation of pigments is generally very difficult to obtain only through visual observations, it is essential the role of the spectrophotometers. A standard method for the specification of colour stimuli had been developed from the *Commission Internationale de l'Eclairage* [13], and has been globally accepted as basis of colorimetry [23].

Therefore, in the study of paintings, spectrophotometers are useful for pigments characterisation, control of the conservation state and evaluation of the pigments' colour before and after conservation interventions [3, 7, 23].

---

[13] CIE - International Commission on Illumination

Experimental conditions - Colorimetric data were collected with a spectrophotometer DataColor Check Plus II (Lawrenceville, NJ), equipped with an integrating sphere. During the analysis, the following parameters were used: diffuse illumination 8°viewing (in accordance with the CIE standard No. 15.2. Colorimetry), SCE and standard Illuminant / Observer D65 / 10 °. The used aperture size was UXAV (ø 2.5 mm) due to small colour details. The results obtained in the CIE L*a*b* chromatic space, defined by the International Commission on Illumination (CIE) in 1976, are the average of three measurements.

FORS

Fiber Optics Reflectance Spectroscopy (FORS) is a powerful, non-invasive, portable technique used for pigments identification [3, 13, 18].

A FORS spectrum reports the ratio between the intensity of the reflected light and the incident light for each wavelength, observed against a standard white reference. The FORS spectra can provide important information on the chemical nature of the material tested, which are useful for the characterisation of the pigments when a comparison of the spectral features (characteristic wavelength) and a spectral database is possible [13].

Experimental conditions - In order to identify the pigments, FORS analysis were performed using a LR1-compact spectrometer (ASEQ instruments, Vancouver, Canada) equipped with a Toshiba TCD 1304DG linear array detector in the range of 300-1000 nm with a spectral resolution < 1 nm (with 50 μm slit). Other specifications of the analysis are here reported: A/D resolution 14 bit; signal to noise ratio 300:1; exposure time 2.5 ms-10 s; CCD reading time 14 m. A Fibre optMA905 to 0.22 numerical aperture single-strand optical fibre was used for the measurements and the results were treated with Lab View software.

EDXRF

X-Ray Fluorescence (XRF) is a rapid and non-invasive technique, used to determine the elemental composition of materials. Especially with a portable handheld equipment (h-XRF), this technique is useful in mural paintings studies, allowing *in situ* analysis, and providing information which serve as primary indicators for pigments identification [31, 33, 38].

In general, when an atom is exposed to X-rays, electrons can be expelled from the inner orbitals because of the high energy of the incident radiation. These electrons create core holes in the excited atom, that can decay either by Auger emission or by X-ray fluorescence [15].

The letter is a phenomenon that occurs when a secondary electron decays to fill the core hole emitting an X-ray photon. The emitted radiation has an element-characteristic energy equal to the difference in energy between the two orbitals involved in the electronic transition. Since each atoms has orbitals with a characteristic energy, by measuring the energy of the fluorescence photon it is possible to identify the emitting atom, as in energy dispersive analysis (EDX) [27].

Experimental conditions - Elemental analysis of the paint layers were carried out *in situ* through Energy Dispersive X-Ray Fluorescence (EDXRF), using a portable *Bruker Tracer III-SD* spectrometer. The instrument was equipped with a Rh excitation source and an X-Flash ® SDD detector. The measurements were made without any filters and obtained with 40 kV high voltage, a current of 30 μA and an acquisition time of 60 s. The obtained spectra were treated with Bruker ARTAX © software.

FTIR

Fourier Transform Infrared Spectroscopy (FTIR) is the most common technique in infrared spectroscopy [16]. In general, IR spectroscopy exploits the capacity of molecules to absorb those radiation frequencies that match with the vibrational frequencies typical of their structures. With this technique, therefore, it is possible to observe different functional groups by monitoring their vibrations [36].

When an infrared photon is absorbed by a molecule, it passes from its fundamental vibrational state to an excited vibrational state. In a typical infrared spectrum, in the abscissa we find a scale of frequencies expressed in wave number, that is quantity of waves per centimetre, and in ordinate the percentage of transmittance [36]. If a material is transparent to infrared radiation, its spectrum will be represented by a line parallel to the abscissa axis. On the other hand, if a material is not completely transparent, absorption and therefore transitions between vibrational energy levels will occur. In this second case the recorded spectrum will be characterized by a series of peaks of varying height for each transition [36].

FTIR is widely used for the study of mural paintings [24, 32, 38] since both organic and inorganic compounds present characteristic absorptions in the mid-IR range (4000-400 cm^{-1}). Binders and fillers can be easily identified with this technique and databases of spectra for pigments components are currently available [34].

Experimental conditions - The analysis of pigments and binders was carried out with the portable mid-infrared *Bruker Optics*® FT-IR spectrometer in combination with *Alpha-R*™reflection module. The built in video-camera allowed to control the measurement area and the exact positioning of the spectrometer. The sample spot size was about 3 mm in diameter to get a higher spatial resolution.

The IR spectra were acquired in the 4000-350 cm^{-1} range, with a spectral resolution of 4 cm^{-1}. The *OPUS 6.5 Bruker* program was used for the processing and treatment of spectra.

ATR-FTIR analysis, on the other hand, were made using the spectrometer equipped with an Attenuated Total Reflection (ATR) accessory (diamond crystal). The spectra were collected in the 4000-350 cm^{-1} range, at a resolution of 4 cm^{-1} and a total of 128 scans.

3.3.2 Micro-invasive techniques

Micro-sampling

Twenty-eight micro-samples were collected from the borders of the fragments with the use of a scalpel with a blade n. 15, in order to carry out additional analysis, aiming at characterising pigments and binders.

The areas selected for the micro-sampling presented a poor state of conservation (lacunae, cracks, etc.), in order to cause the minimum impact possible on the materials. The dimension of the micro-samples scrabbled from the paint surface was less than 0.5 mm and their weigh was under 1 mg. Table E.1 in Appendix E shows the location of the micro-sampling.

Micro-FTIR

Experimental conditions - Pigments identification was carried out through micro Fourier Transform Infrared Spectroscopy (μ-FTIR) using a Bruker Tensor 27 Mid-IR (MIR) spectrometer. The spectrometer is coupled with a HYPERION 3000 microscope and controlled by the OPUS 7.2 software (Copyright© 2012 Bruker Optics and Microanalysis GmbH, Berlin, Germany). The MCT (Mercury Cadmium Telluride) detector cooled with liquid nitrogen allows the spectra acquisition in different points of the micro-sample. The μ-samples were analysed in transmission mode using a 15x objective and an EX'Press 1.6 mm diamond compression micro-cell, STJ-0169. The IR spectra were plotted in the region of 4000-600 cm $^{-1}$ with 64 scans and 4 cm $^{-1}$ spectral resolution. In order to identify the compounds present in the 28 μ-samples, 70 micro analysis were performed to ensure the reproducibility and consistency of the results.

Micro-XRD

X-rays are electromagnetic radiations with wavelengths produced when any electrically charged particle of sufficient kinetic energy is rapidly decelerated. When an X-ray strikes an electron (the scatterer) of an atom, secondary spherical waves of the same energy of the incident ones are emanated from the scatterer. This phenomenon is called elastic scattering and, in particular conditions, it can originate a diffracted beam [27]. Diffraction can be considered a scattering phenomenon in which a large number of scattered rays are in phase and can produce a constructive interference. The existence of this particular phase relation between scattered waves depends on the difference in path length covered by the incident beam. To have a constructive interference, this difference has to be an integral multiple (represented by the reflection order n) of the wavelength of the incident ray (λ), as shown in the Bragg equation:

$$2dsin\theta = n\lambda \tag{3.1}$$

where the first term is the path difference and depends on the incident angle θ, that has to be equal to the diffraction angle. If atoms are randomly arranged in the space, the scattering occurs in all directions and diffraction conditions are not present. On the other hand, if atoms are arranged in a regular lattice (like in crystals), constructive interferences occur and diffraction beams can be seen at angles that respect the Bragg law. For other directions the elastic scattering is not visible, since scattered waves are added in a destructive way [14].

By measuring the intensities of the diffracted beams as a function of the angle 2θ between them and the incident X-ray, it is possible to obtain a diffraction pattern characteristic of the studied compound. In combination with the Bragg law, this diffraction pattern gives information on unit cell characteristics and atom positions in the crystal lattice [14, 27, 34].

In particular, in the study of mural paintings, X-Ray Diffraction (XRD) is a useful analytical technique for the characterisation of inorganic pigments. It is particularly efficient for the discrimination and identification of specific pigments which present the same chemical composition, but different crystalline phases [2, 18, 34].

Experimental conditions - Micro-X-ray diffraction analysis was conducted using a *Bruker*™ *D8 Discover*®diffractometer, equipped with a Cu Kα radiation source (40 kV, 40 mA), a Göebel mirror, a 1 mm collimator and a LYNXEYE linear detector, acting as 192 individual detectors. The XRD patterns were acquired at a 2θ angular range of 3-75 °, with a step size of 0.05 °and a step time of 1 seconds. The identification of crystalline phases was performed with the DIFFRAC.SUITE EVA ®software using the Powder Diffraction File (PDF-2) X-ray patterns database of the International Centre for Diffraction Data (ICDD).

Chapter 4

Results and discussion

In this chapter, the main results of the analyses carried out on the selected mural painting fragments will be presented and discussed. A specific exam worksheet was created for each fragment analysed, containing all the data acquired during the analysis. One of the most representative worksheets done during this study is reported in the last part of the Appendix.

4.1 Pigments characterisation

Colour measurements of 144 points were performed *in situ* on the different fragments, in order to obtain an objective colour evaluation of the chromatic palette.

In the figure (Figure 4.1) is provided an overview of the current chromatic palette of the 56 mural painting fragments, showing the results of the 144 measurements carried out. The diagram is reported on the CIE a*b* colour space, in which a* (0-100) corresponds to the red (+a*) and green (-a*) chromatic coordinates, while the b* (0-100) represents the yellow (+b*) and blue (-b*) components [16].

The colorimetric measurements give an overall visual perspective of the colours analysed. From the diagram, in fact, it is evident the majority of yellow and red paint layers, together with some green and few blue ones; some measurements show greater values (e.g. the ones encircled in the graph), indicating a higher intensity of their colour.

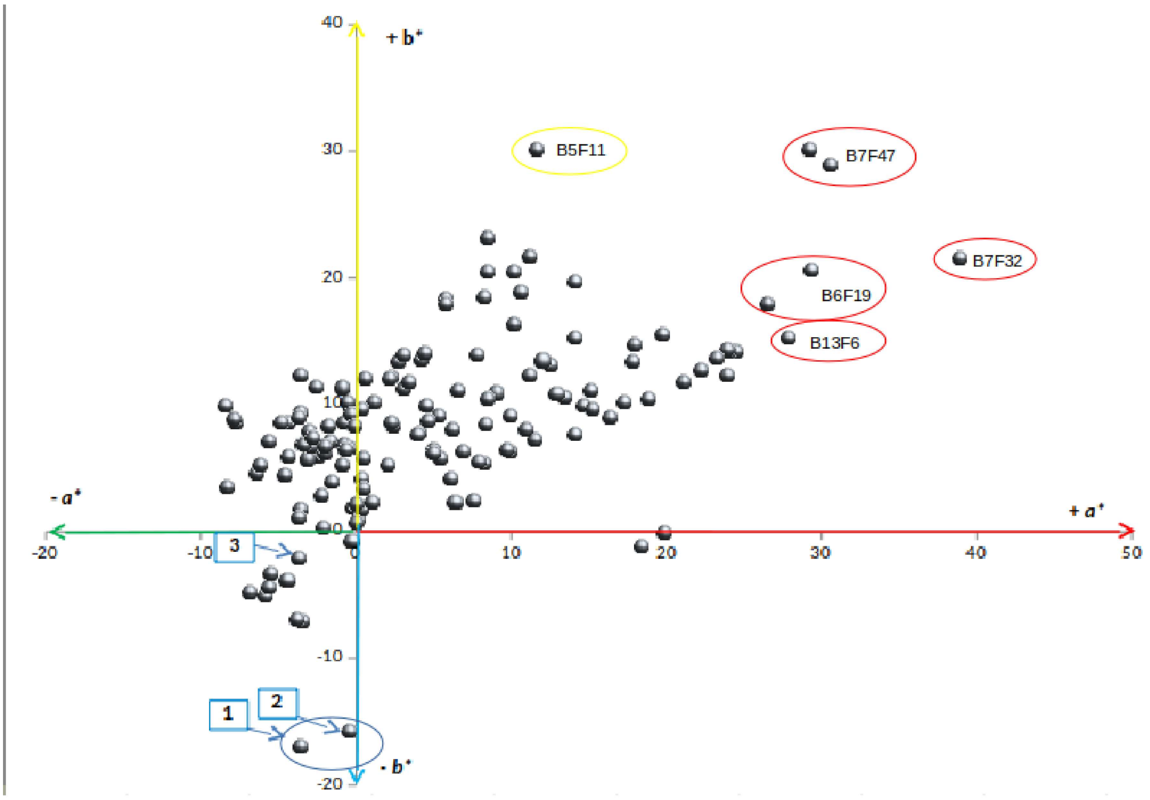


Figure 4.1: Global view of the 144 paint areas analysed, in the bidimensional CIE a*b* colour space.

Moreover, at the same intensity, two colours can be distinguished due to their different chromatic components. The three points pointed out by an arrow in the graph, for example, correspond to the measurements carried out on the samples B2F12 (1), B18F2 (2) and B7F9 (3). As indicated by their colour measurements reported in Table 4.1, the first one presents an a* value higher than the second one, which means that the green component is lower (i.e. the blue layer presents some red traces on the surface contrasting the green component). Moreover, both the first and second samples present a blue hue (h value) much more intense than the blue layer of the third sample. These results are due to the different nature of the pigments that is strictly linked to their colorimetric behaviour. Together with the colorimetric analysis in the CIE colour system, the diffuse reflection spectral curve of each paint layer was also acquired in the visible range (360-750 nm).

Generally, when observing paint layers by sight, it is not possible to distinguish the nature of different pigments. However, in some cases, when looking at their diffuse

Table 4.1: CIE parameters of the three considered samples B2F12 (1), B18F2 (2) and B7F9 (3).

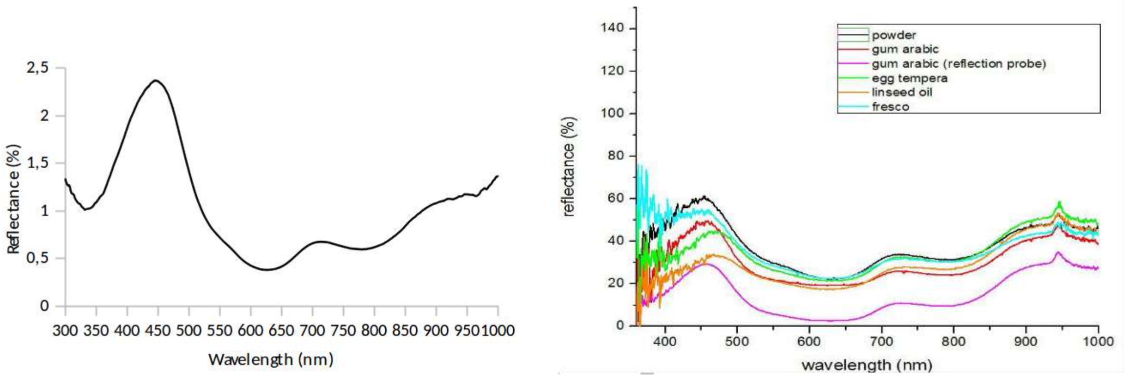
Sample	CIE *a*	CIE *b*	CIE *h*
1 	-0.39	-15.79	268.60
2 	-3.61	-16.90	257.94
3 	-3.68	-2.08	209.44

reflectance spectral curves, the differences between them can be evident.

Spectral curves record the absorption or reflection of the light at different wavelengths of the visible spectrum, depending on the composition of the material analysed: their shape can be characteristic, and sometimes unique, for some colourants (pigments or dyes) [23].

A similar result can be obtained by means of FORS technique, with the main difference being the wider range of acquisition (300-1000 nm). The spectra acquired in this range include a small portion of the near infrared and near ultraviolet, in which some characteristic peaks can be detected. When compared with reference databases, also available on-line [13], these reflectance spectral curves enable the identification of well-defined pigments. A clear example of the great potential of the spectral curves in pigments identification will be presented in the section dedicated to blue pigments.

The elemental analysis of the pigments was performed with a handheld XRF spectrometer. The spectra were acquired mainly on the same coloured areas analysed by spectrophotometry.



(a) B18F2 - FORS reflectance spectral curve.

(b) FORS standard spectra of Egyptian blue.

Figure 4.2: Comparison between experimental and standard results.

A qualitative investigation carried out on the totality of the acquired spectra, found out that strontium and calcium are present in all the paint layers analysed, probably deriving from the calcite ($CaCO_3$) in the support. Since strontium and calcium have similar chemical properties (same valence and similar ionic radius), Sr is commonly found as substitute of Ca in all the Ca-rich phases [16].

The analytical results about the studied paint layers are shown below. They were grouped into four main colours (blue, red, yellow and green) according to the colorimetric data.

4.1.1 Blue pigments

The great potential of the use of spectral curves in pigments identification can be illustrated through a clear example concerning the calcium copper silicate, also known as Egyptian blue. The spectral curve of this pigment presents two absorption bands near 630 nm and 800 nm, together with a characteristic peak around 950 nm [13], probably caused by its infrared fluorescence [1]. In the Figure 4.2(a) is reported the reflectance spectral curve acquired between 300 and 1000 nm by means of spectrophotometry of the sample B18F2, coming from Egypt. The curve was compared with the standard spectra of the Egyptian blue from literature[1] [13] (Figure 4.2(b)).

The similar shape of the two curves can be easily noticed and the absorption

---

[1] https://chsopensource.org/egyptian-blue-k-10060/

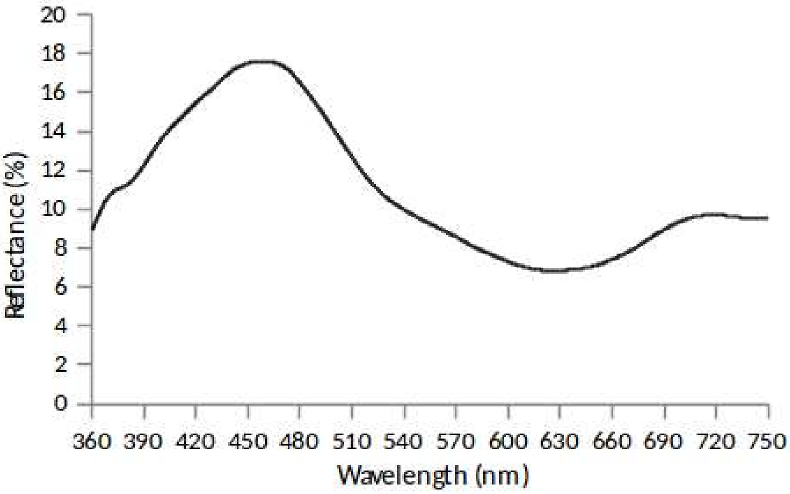


Figure 4.3: B18F2 - Diffuse reflectance spectral curve (360-750nm).

and reflection bands typical of this pigment are present. Otherwise, the spectrum acquired by spectrophotometer in a narrower range (Figure 4.3), does not show the characteristic peak at 950 nm and, therefore, it is not discriminating.

From the elemental analysis of the 6 blue paint areas (Figure 4.4), two different patterns were identified, according to the main elements present. In the first type, iron (Fe) was detected, while in the second one silicon (Si) is present. As expected, copper (Cu) is present in most of the blue paint layers, as the main chromophore.

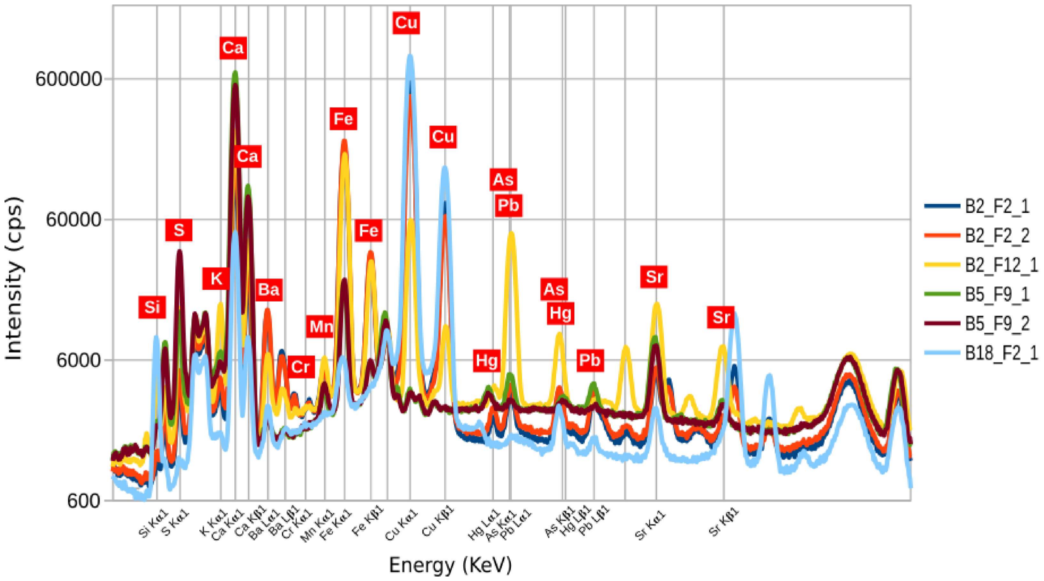


Figure 4.4: EDXRF spectra of 6 blue paint areas.

Table 4.2: B18F2 - EDXRF elemental analysis of the blue paint layers.

Element	Line	B18F2-1	B18F2-2	B18F2-3
Si	K12	1,560	1,523	1,597
K	K12	0,067	0,157	0,094
Ca	K12	10,816	10,972	11,284
Mn	K12	0,051	0,053	0,043
Fe	K12	0,869	0,898	0,872
Cu	K12	250,204	262,489	261,891
Sr	K12	0,620	0,660	0,619
Rh	K12	1,000	1,000	1,000

The only elemental analysis of a blue area revealing a high content of copper together with silicon is reported in Table 4.2 and it is relative to the sample B18F2 (Figure (2) in Table 4.1). This sample is the small blue ball of Egyptian blue, already identified by means of FORS, as shown at the beginning of this paragraph. EDXRF analysis served in this case as the final evidence for the characterisation of this pigment.

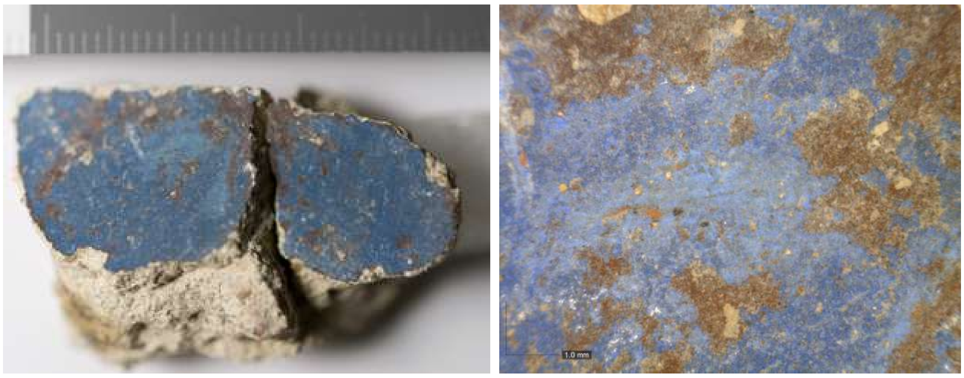
Egyptian blue is a calcium copper silicate, synthetic form of the very rare mineral cuprorivaite, with formula $CaCuSi_4O_{10}$ [16, 22]. It is believed to be the earliest pigment synthesised in human history, first developed in the early dynastic period in Egypt (around 2500 BC) [9, 16, 22]. It was the most extensively used blue pigment in Egypt and in the Mediterranean basin until the end of the Roman period and beyond [9, 16]. Its employment in Italy and Roman sites, during the Etruscan and Roman periods, is proven by findings of many samples of unused pigment, as well as by its employment on wall paintings, evidence of the common use of this pigment among Roman painters [29]. Since this pigment is very stable, it does not show any change of colour, even after thousands of years of exposition to sun and heat, as for example on Egyptian monuments [9, 16]. It can occur also mixed with other pigments, like green earth or ochres, and because of its composition, no reactions between the different pigments take place [29].

Table 4.3: B2F2 - EDXRF elemental analysis of the 2 blue paint layers.

Element	Line	B2F2-1	B2F2-2
Si	K12	0,067	0,075
K	K12	0,250	0,327
Ca	K12	26,385	32,324
Mn	K12	0,593	0,530
Fe	K12	47,683	47,227
Cu	K12	145,454	107,322
Sr	K12	1,656	1,502
Rh	K12	1,000	1,000
Ba	K12	0,010	0,003
Ba	L1	2,536	2,470

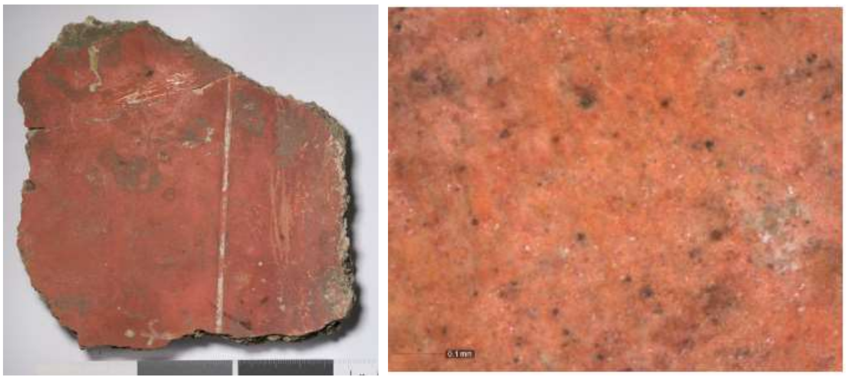
Another singular case among the blue pigments is the fragment B2F2 shown in Figure 4.5. Its elemental composition reveals the presence of high amount of copper (Cu), together with iron (Fe) and calcium (Ca), as reported in Table 4.3.

The curious element in this case is iron, usually not related to blue pigments. However, when looking at the optical microscope images of the sample at 60x magnification, the brownish layer underneath the blue one is evident (Figure 4.5(b)). It is credible, then, that the content of iron derives from the brown underlay, while the



(a) B2F2 - Fragment overview. (b) B2F2 - OM Vis image (60x).

Figure 4.5: Fragment B2F2.



(a) B13F3 - Fragment overview. (b) OM Vis image (435x).

Figure 4.6: Fragment B13F3.

copper can be associated to a blue copper- based pigment.

4.1.2 Red pigments

In this study, mainly two kinds of red pigments have been most frequently detected in the analysed fragments: red ochre and vermilion.

In the red fragment B13F3 shown in Figure 4.6, for example, the pigment identified was vermilion. Mercury sulphide pigments, such as vermilion (HgS), own a high light-scattering power due to their high refractive index [26]. Because of its chemical nature, vermilion absorbs light at 400 nm to about 570 nm. Its reflectance spectral curve is then characterised by a sharp slope between 605 and 615 nm [27], clearly visible in the example of the fragment B13F3 (Figure 4.7).

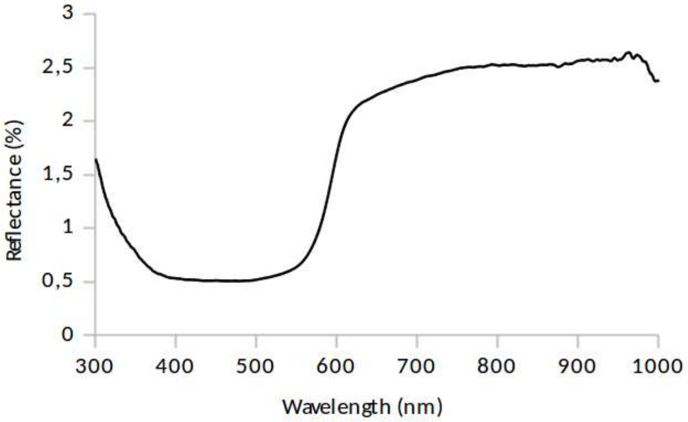
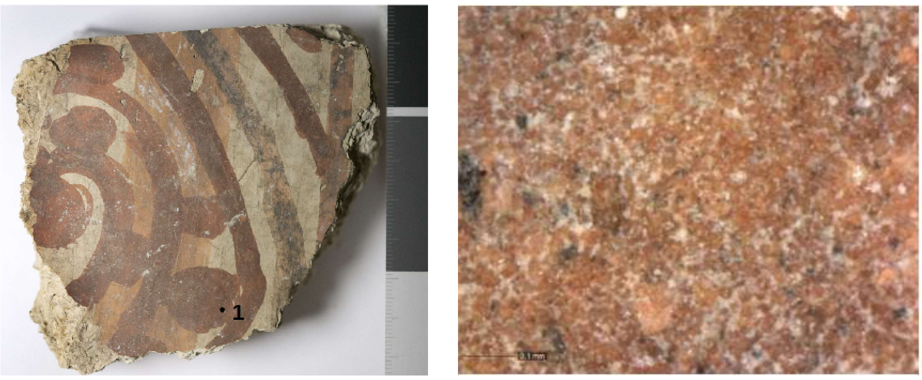


Figure 4.7: B13F3 - reflectance spectral curve (FORS).



(a) B2F6 - Fragment overview with indication of colorimetric and spectrophotometric analysis of point 1.

(b) B2F6 - OM Vis image of the point 1 (435x).

Figure 4.8: Fragment B2F6.

Vermilion has been used as pigment since ancient times and, in particular, it was very popular among the wealthy people during the Roman period [20, 23]. Considered as a luxury commodity, vermilion was seen as a sign of the financial and social power [23] and because of its high price, it was not used as much as red ochre, which was a lot cheaper.

Red ochre pigments belong to the large family of ochres, also known as earth pigments. Their wide range of colours spreads from yellow to orange, to red and to violet, depending on their chemical and mineralogical composition [17]. Earth pigments contain a variable amount of iron oxides (hematite and goethite), together with alumino-silicates, quartz and calcium compounds. When the hematite (Fe2O3) is the main iron oxide, then the material shows a red colour (red ochre). On the other hand, when goethite (FeOOH) is predominant, the ochre is yellow [17]. The chemical process responsible for these colours is the charge transfer between the ion Fe^{3+}, contained in both oxides, and its ligands O^{2-} or OH^{-}. Because of this transition, ochres strongly absorb in the blue-green range of the visible spectrum. This is reflected in their diffuse reflectance spectrum of sample B2F6 (represented in Figure 4.8), which shows a sharp slope around 570-590 nm and a maximum around 750 nm [21] (Figure 4.9).

A confirmation of the preliminary identification through spectro-colorimetry and

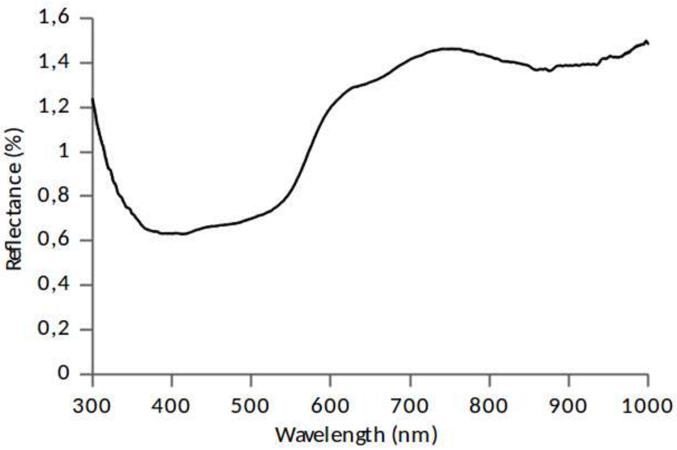


Figure 4.9: FB2F6 - reflectance spectral curve (FORS) of the point 1.

FORS, was then looked for by means of EDXRF analysis. When looking at the totality of red pigments, the main elements detected are Fe, Hg and Pb. In particular, X-rays fluorescence results have indicated two main patterns in the elemental compositions of the red paint layers. As expected from the spectral investigation, the pigments identified were mainly red ochre and vermilion.

The first one was recorded in the majority of the red paint layers analysed (Figure 4.10) and it was characterised by the high content of iron (Fe). Other elements such as potassium (K), silicon (Si), manganese (Mn) and titanium (Ti) were also found in lower amount.

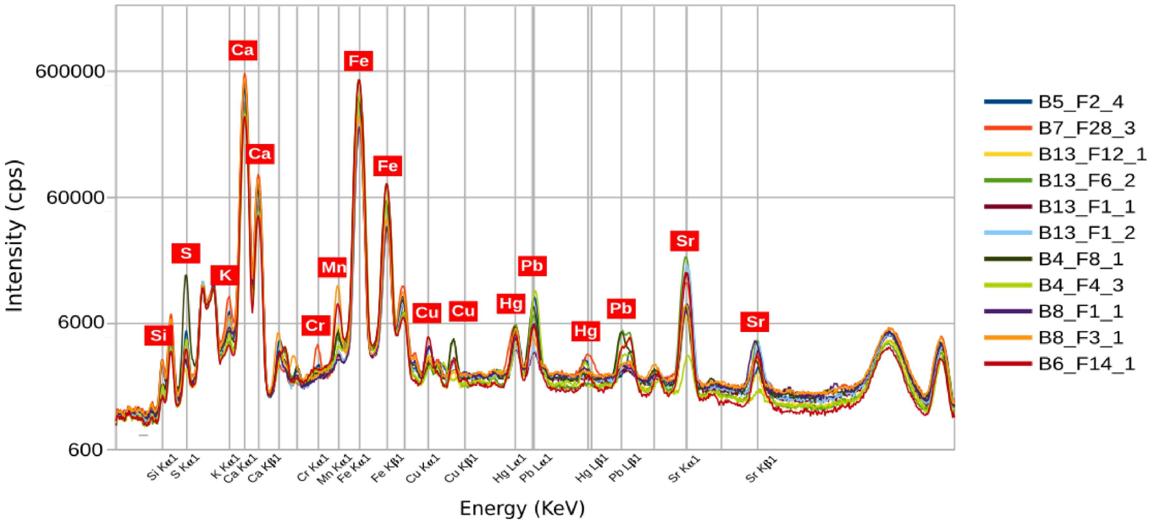


Figure 4.10: EDXRF spectra of red samples containing iron.

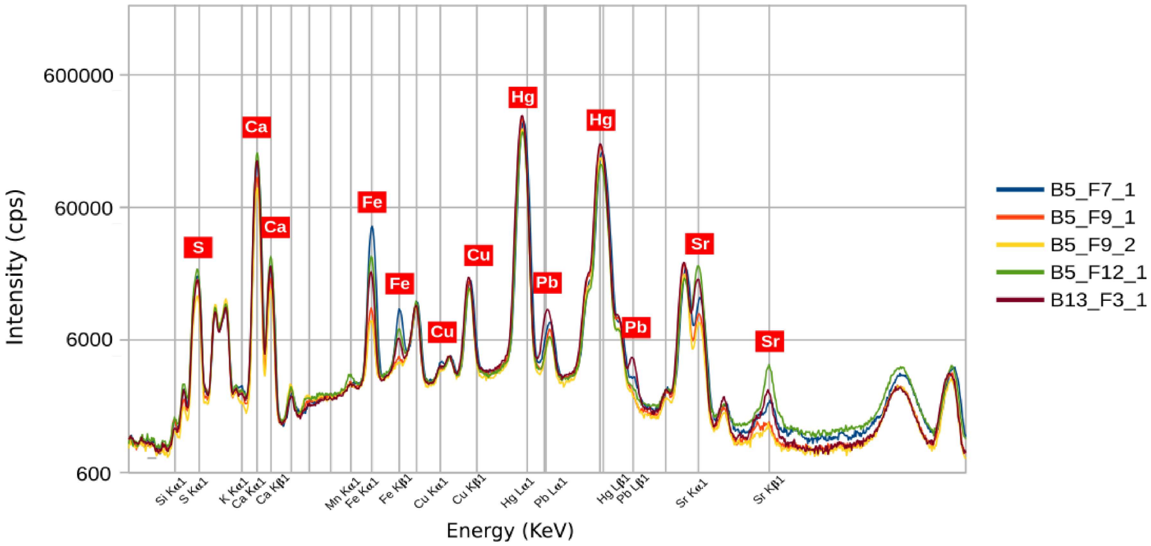


Figure 4.11: EDXRF spectra of red samples containing Hg and S.

The second red pattern was identified by the high amount of mercury (Hg), characteristic element of cinnabar, together with sulphur (S) and it was revealed clearly in 4 samples (Figure 4.11). The elemental composition of these red paint areas was revealed by EDXRF and is reported in Table 4.4.

Table 4.4: EDXRF elemental analysis of the red paint layers containing Hg and S.

Element	Line	B5F4-1	B5F5-1	B5F5-2	B5F9-1	B13F3-1
S	K12	1,140	1,055	0,346	0,544	1,229
Ca	K12	20,257	15,908	15,625	24,408	21,190
Mn	K12	0,107	0,123	0,132	0,185	0,104
Fe	K12	7,154	1,509	1,452	4,319	3,191
Cu	K12	0,198	0,125	0,261	0,155	0,150
Zn	K12	0,293	0,274	1,838	0,397	0,386
As	K12	1,352	1,025	1,002	0,858	1,978
Sr	K12	2,199	1,504	1,166	4,868	3,554
Rh	K12	1,000	1,000	1,000	1,000	1,000
Hg	L1	57,986	64,275	61,978	50,602	66,997
Hg	M1	1,439	1,496	1,601	1,771	1,314

Figure 4.12: Sample B7F47.

In addition to these two main groups of red pigments, two singular cases were identified. The first particular composition was revealed on one single fragment, the B7F47 (Figure 4.12). The h-XRF analysis of this fragment revealed a very high concentration of lead (Pb) and calcium (Ca) (Figure 4.13) and is reported in Table 4.5. Due to the observed bright orange colour of the fragment and because of its elemental composition, the presence of minuim was hypothesised.

This pigment, also known as red lead, is supposed to be one of the earliest pigments produced artificially. The term minium comes from the naturally occurring mineral with formula Pb_3O_4 and it was applied to the artificial pigment since classical times.

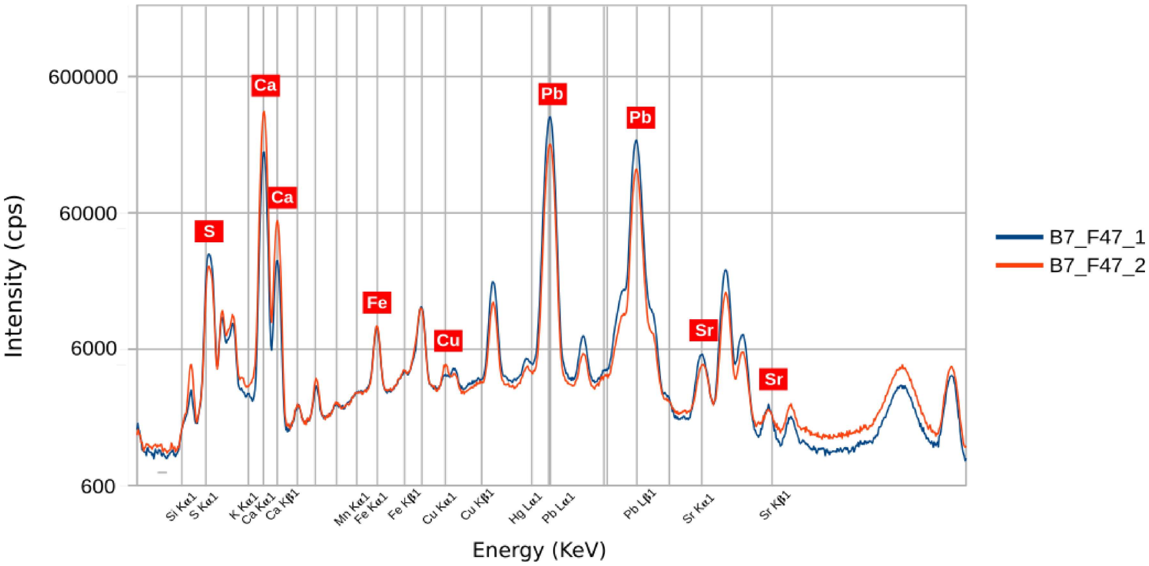


Figure 4.13: EDXRF spectra of the fragment B7F47.

Table 4.5: EDXRF elemental analysis of the fragment B7F11.

Element	Line	B7F11-1	B7F11-2
Si	K12	0,589	0,688
S	K12	0,053	0,072
K	K12	1,573	1,467
Ca	K12	30,544	26,045
Mn	K12	0,860	0,503
Fe	K12	17,154	17,594
Cu	K12	3,309	4,619
Sr	K12	1,875	1,757
Rh	K12	1,000	1,000

Red lead is characterised by a bright red orange colour which has a tendency to darken when exposed to air [22]. However, in the case of fragment B7F47, the chromatic aspect of the paint layer does not show any trace of darkening. The undoubted identification of this pigment was possible thanks to micro-XRD analysis, which revealed in the diffractogram (Figure 4.14) the presence of the mineral minium together with calcite.

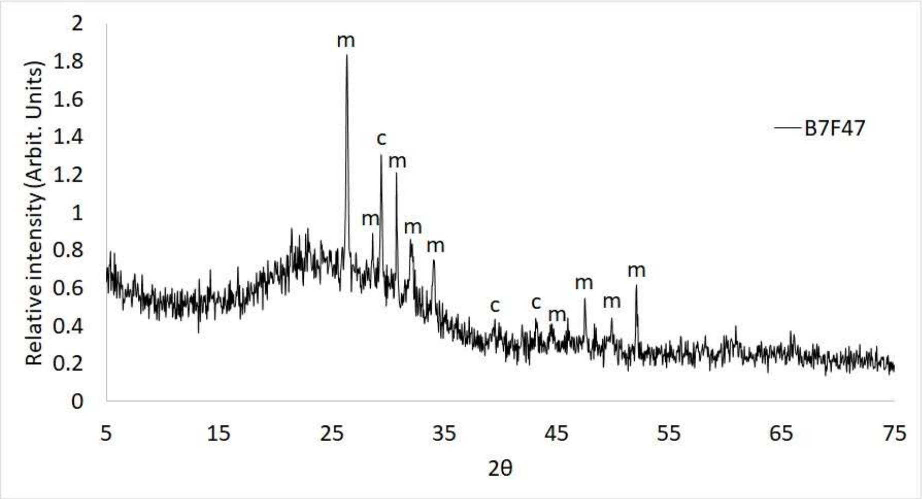


Figure 4.14: B7F47 - X-Rays Diffractogram showing characteristic peaks of minium (m) and calcite (c).

(a) B7F11 - Fragment overview. (b) B7F11 - OM Vis image (435x).

Figure 4.15: Fragment B7F11.

The second peculiar chemical composition identified among the red pigments was relative to the fragment B7F11 (Figure 4.15). Its elemental composition revealed a high content of iron (Fe), together with copper (Cu) and a low amount of silicon (Si) (Table 4.5).

The presence of copper and silicon in a red sample could not allow a clear identification of the pigment, in a first moment. When pigments mixtures are present, such in this case, the observation with optical microscope can be crucial. The photos of the fragment B7F11 taken with the portable digital microscope in 60x and 435x magnification, show clearly some blue particles in a pink ground (Figure 4.15). In this case, probably, Egyptian blue ($CaCuSi_4O_{10}$) was added to a earth pigment, common practice followed in order to vary the hue of the base pigment. The presence of a mixture with Egyptian blue in this pink paint layer was confirmed by the micro-FTIR results, reported in Appendix F.

4.1.3 Yellow pigments

Among the 88 yellow paint layers analysed, the main element detected by EDXRF was Fe, together with Ca, similar to the spectra of the red ochres.

Yellow ochre is a hydrated iron hydroxide ($FeO(OH) \cdot H_2O$) and it belongs to the family of the natural earth clay pigments [22]. Same as red ochre, it can be well identified by its elemental composition and reflectance profile. The elements that

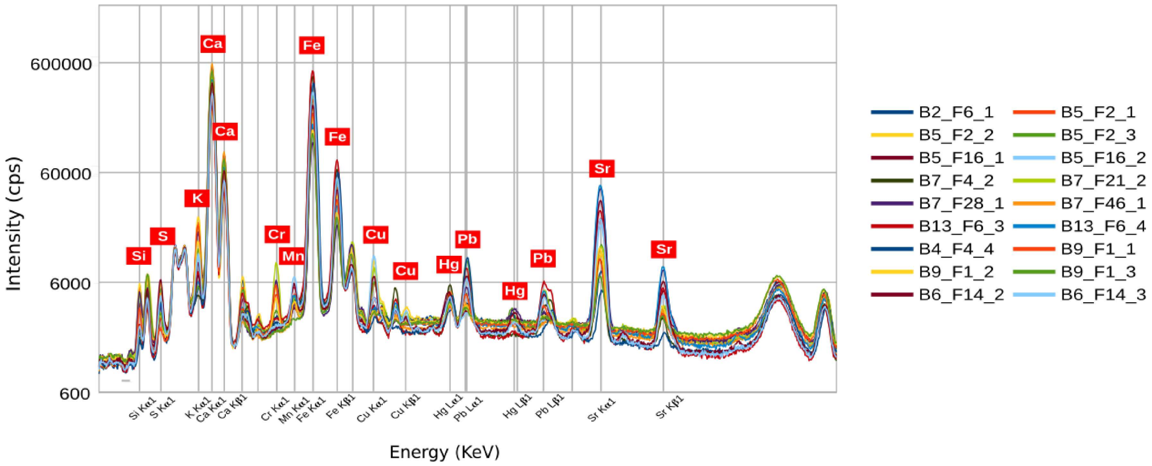


Figure 4.16: EDXRF spectra of yellow paint areas containing iron.

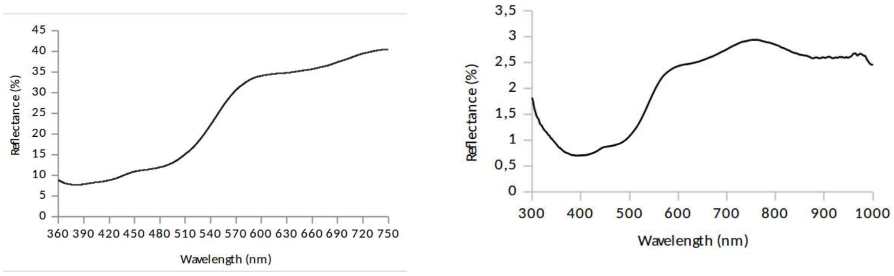
characterise this pigment, together with iron (Fe), are calcium (Ca), silicon (Si), aluminium (Al) and potassium (K) and it was identified thanks to h-XRF analysis (Figure 4.16).

The diffuse reflectance spectral curve of these pigments shows the same ”curving, rising, long-wavelength tail” characteristic of iron oxides, not so evident as in the red ochres but still apparent [23]. The ”s-shape” characteristic of iron-containing pigments [12] is visible, as well as the two broad absorbance bands near 660 and 930 nm, attributed to goethite (FeO(OH)), the chromophore mineral of the brown ochre [17]. Spectral curves of the fragment B5F16, visible in Figure 4.17, are here reported

(a) B5F16 - Fragment overview with indication of point of analysis.

(b) B5F16 - OM Vis image (435x) of point 1.

Figure 4.17: Fragment B5F16.



(a) B5F16 - Diffuse reflectance spectral curve of point 1 (360-750).

(b) B5F16 - Reflectance spectral curve of point 1 (300-1000).

Figure 4.18: B5F16 - Comparison between the spectral curves obtained by FORS and colorimetry.

in Figure 4.18 as an example.

4.1.4 Green pigments

In the 13 green paint areas investigated, the elemental analysis carried out with h-XRF indicates the presence of two main chromophore elements, namely copper (Cu) and iron (Fe) (Figure 4.19).

The iron content can be associated to green earth, a natural greyish green pigment. Green earth is a mixture of hydro-silicates of iron, magnesium (Mg), aluminium

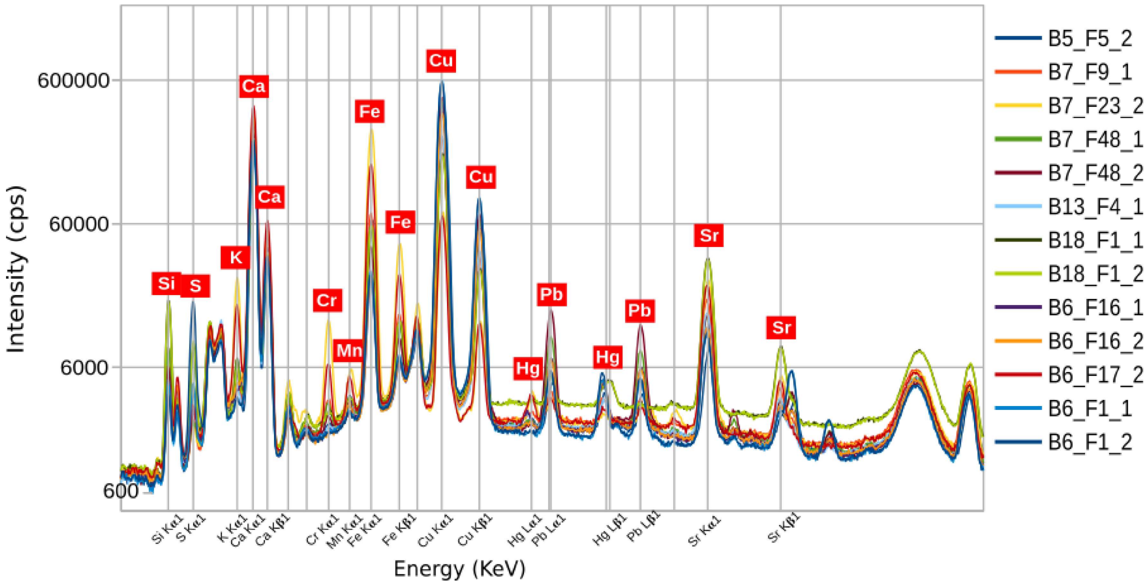
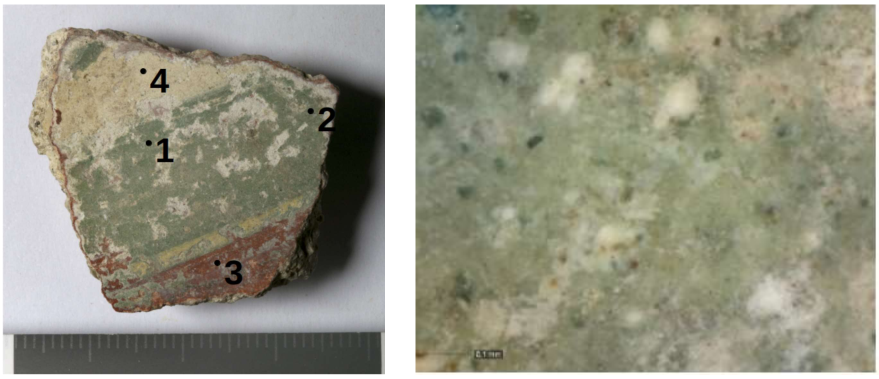


Figure 4.19: EDXRF spectra of green paint areas.



(a) B7F28 - Fragment overview with analysis indications.

(b) B7F28 - OM Vis image (435x) of point 1.

Figure 4.20: Fragment B7F28.

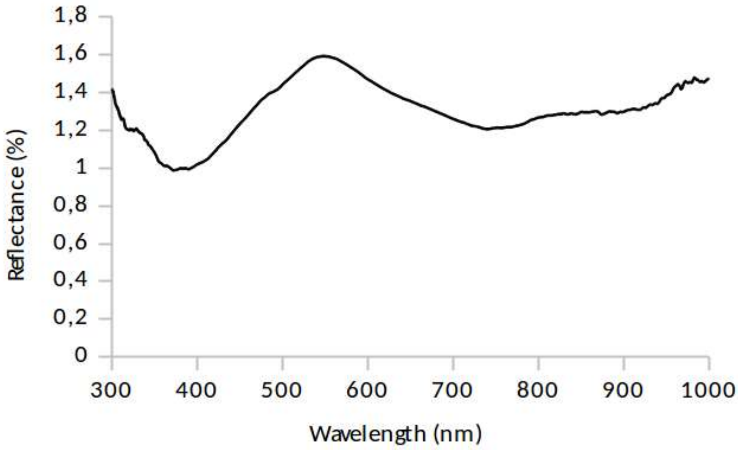
(Al) and potassium (K), consisting mainly of the minerals celadonite and glauconite. These last two minerals belong to the mica group and contain the phyllosilicate group [Si_4O_{10}] coordinated with the above-mentioned metals. The green earth pigment has been widely used all over the world, since antiquity [22].

Green earth was identified in several green areas of the analysed fragments, thanks to the combined use of complementary analytical techniques. The presence of this pigment was found, for example, on the green areas of the fragments B7F28 (Figure 4.20). The reflectance spectral curve of green earth, in the range between 300 and 1000 nm, is characterised by the presence of two broad reflectance maxima near 560 nm and 810 nm, due to the presence of celadonite [9] and they are visible in the example of the fragment B7F28 (Figure 4.21(a)).

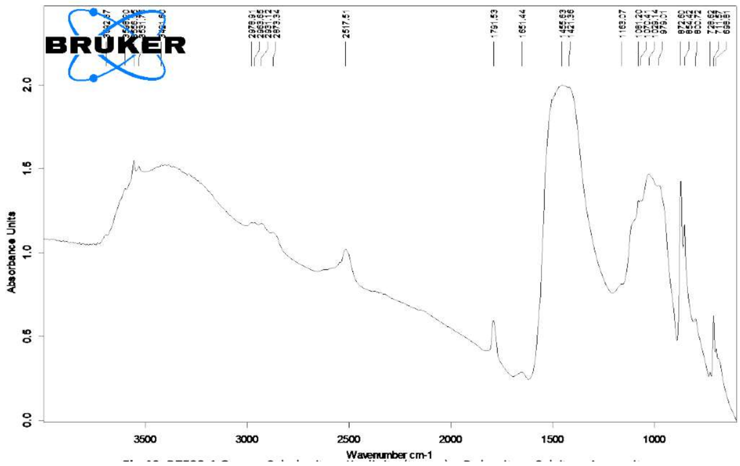
A confirmation of the presence of this pigment was obtained by the μ-FTIR analysis, which revealed the characteristic peaks of celadonite (Figure 4.21(b)).

The remaining green areas are characterised by the presence of copper. In the Table 4.6 is reported the elemental composition of the 6 green areas with a consistent Cu content. The spectra of the same analysis is reported in Figure 4.22.

The analysis of two areas of the fragment B7F23 present a lower amount of copper, compared with the other fragments, as well as a higher amount of iron (Fe). The



(a) B7F28 - Reflectance spectral curve of point 1 (300-1000nm).



(b) B7F28 - FTIR spectrum relative to point 1, showing characteristic peaks of celadonite, calcite, gypsum.

Figure 4.21: Fragment B7F28.

silicon (Si) was revealed too, slightly higher in the two analysed areas of the fragment B18F1 (coming from Egypt), probably deriving from a mixture with Egyptian blue.

The copper content can be related to the copper carbonate malachite with formula $Cu_2CO_3 \cdot Cu(OH)_2$, a green pigment commonly used since ancient times [20].

At the same time, the copper content can derive from Egyptian blue ($CaCuSi_4O_{10}$), which could have been used to obtain the green colour. From the literature [2], it is known that in Roman times, around Pompeii and Herculaneum, the synthetic calcium copper silicate was the main component of green-appearing mural paintings: green pigments, like green earth and malachite, were added, together with ochres,

Table 4.6: EDXRF elemental analysis of green paint layers containing Cu.

Element	Line	B7F9-1	B7F48-1	B18F1-1	B18F1-2	B7F23-1	B7F23-2
Si	K12	0,861	0,931	1,466	1,361	0,661	0,751
S	K12	0,091	0,087	0,605	0,628	0,046	0,050
K	K12	0,607	0,685	0,345	0,345	3,102	3,199
Ca	K12	34,742	36,927	23,523	23,204	42,158	38,264
Cr	K12	0,204	0,179	0,052	0,060	1,519	1,697
Mn	K12	0,123	0,090	0,093	0,102	0,302	0,302
Fe	K12	11,134	9,508	6,454	6,531	43,027	46,354
Cu	K12	41,217	79,257	24,099	22,423	12,016	12,802
Sr	K12	3,630	2,806	5,584	5,256	6,403	5,414
Rh	K12	1,000	1,000	1,000	1,000	1,000	1,000

to the Egyptian blue. The latter constituted the main component of the green mix, since it was largely produced in that territory and hence it had a lower price [2].

A discrimination between these pigments, or mixtures of pigments, can not be conclusive only by means of elemental analysis, since they both present copper as the main chromophore element. Also in this case, the μ-FTIR analysis led to a clear conclusion and, again, the importance of using complementary analytical techniques is underlined. The IR spectra, in fact, revealed the presence of materials, such as

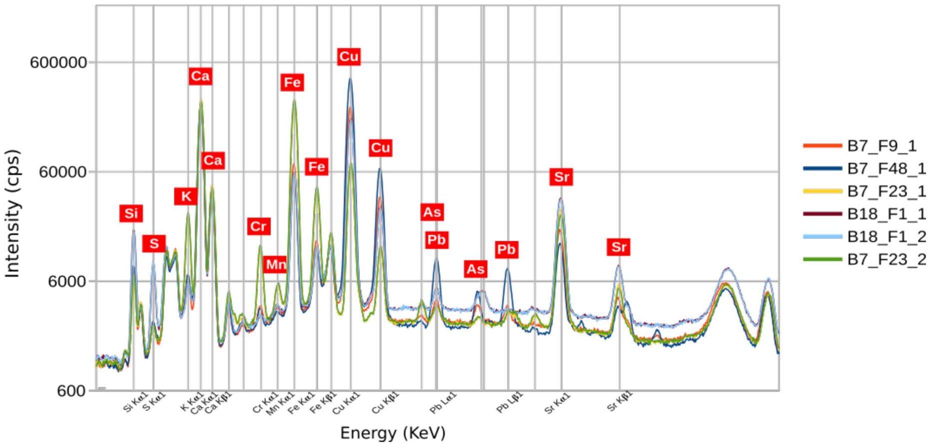
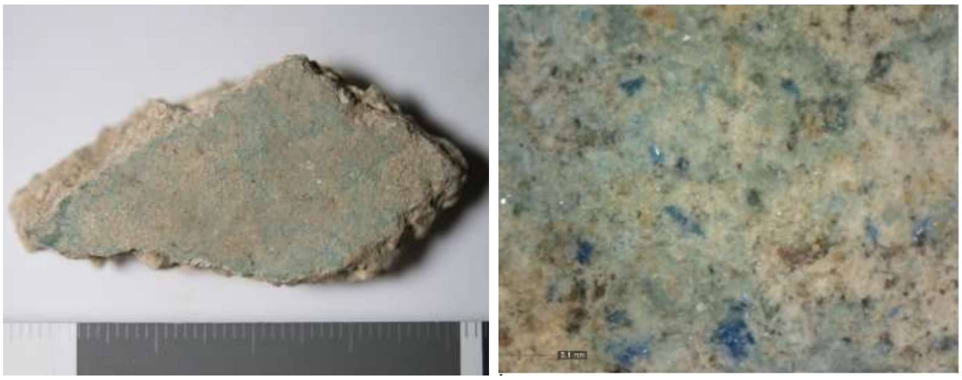


Figure 4.22: EDXRF spectra of green areas containing Cu + Si.



(a) B7F23 - Fragment overview. (b) B7F23 - OM Vis image (435x).

Figure 4.23: Fragment B7F23.

celadonite or Egyptian blue, which are discriminating factors for the identification of these green areas (Figure 4.21(b)).

In the case of the fragment B7F23 (shown in Figure 4.23), the green area observed with the portable optical microscope at 435x magnification, revealed the presence of yellow and blue particles (Figure 4.23(b)). The μ-FTIR spectrum of the same area identified the presence of celadonite, Egyptian blue, kaolinite, calcite and aragonite, the last two most likely deriving from the substrate (Figure 4.24).

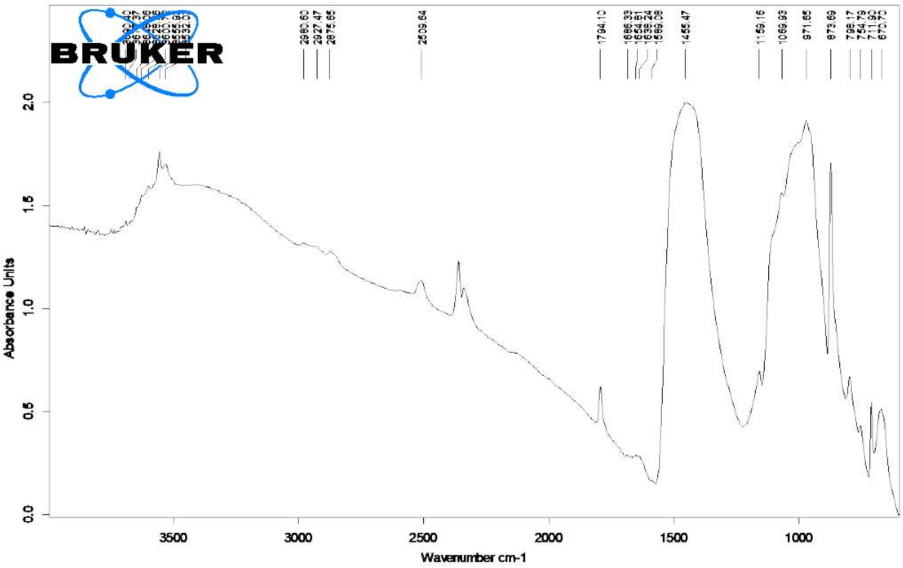


Figure 4.24: Fragment B7F23 - FTIR spectrum revealing Celadonite + Egyptian blue + kaolinite + gypsum + calcite

Through the results of these analyses, it is evident the use of a mixture of blue and yellow pigments to obtain a green hue.

4.2 Binders characterisation

The binding media can be a discriminating factor for the different mural painting techniques. As already described in the section dedicated to the materials, a selection of 15 fragments was analysed by means of μ-FTIR in order to investigate the possible presence of organic materials.

28 micro-samples were collected from the above-mentioned 15 fragments coming from Rome and Pompeii (Appendix E). Since these fragments visually show some characteristics usually found in *a secco* paintings, the identification of organic binders in their paint layers could support the hypothesis that these fragments were painted using *a secco* techniques.

However, μ-FTIR analysis of the micro-samples did not reveal any presence of organic compounds. The only likely binding material revealed in the totality of the samples was calcite (Appendix F).

The absence of organic compounds in the samples, could lead to conclude that the technique used for this mural paintings was not *a secco*. However, it cannot be totally excluded the use of a "lime painting" technique, *a secco* technique which does not require the use of any organic binder [26, 28].

Unfortunately, from these data, the discrimination of the painting technique cannot be possible. In order to obtain a final characterisation, it would be necessary the observation of cross sections of the paint layers. Only by observing the stratigraphic sequences and the distribution of chemical elements, the differences between the two techniques can be revealed, assigning the role of calcite, whether as a binder, or as the main component of the support [28].

4.3 Advantages and limitations of the used analytical techniques

The non-invasive analytical techniques used *in situ* during this research revealed very useful for the characterisation of pigments. Some limitations for each of them are evident, but the combined used of the right techniques lead to important conclusions.

The colorimetry measurements, for instance, are useful to give a clear overall perspective and objective data of the chromatic palette of the fragments analysed. However, some factors can limit the reliability of this analysis, since the colour of a paint layer can be subjected to some changes during the years: possible degradation process of some pigments, as well as accumulations of dirt on the surface, can interfere with the CIE L*a*b* coordinates [23]. The same possible factors can interfere with FORS, another powerful equipment for surface chromatic analysis. On the other hand, the use of portable optical microscope like Dino-lite, can help in the observation of the surface with higher magnifications, allowing the recognition of pigments particles, as well as identifying the presence of pigments mixtures. Moreover, h-XRF allow the identification of elemental composition, but at the same time, this punctual analysis can reach as well the layers under the surface, that can lead to false positive results.

It is here clear the importance of the selection of multi-analytical approaches in the study of mural paintings, and in particular the great potentialities of portable, non-invasive analytical techniques.

One of the main drawbacks obtained through this study is about the portable FTIR.

One of the objectives of this case study was to characterise the pigments and binders by means of portable and non-invasive instrumentation, included FTIR. This latter technique, in particular, was used with the aim of identifying the binders, to check the possible presence of organic compounds.

In situ non-invasive methods using reflection FTIR equipments have already been applied in several studies [5, 25, 30] and this approach was the initially preferred in this research, since it is non-invasive and can preserve the integrity of the samples.

Reflection infrared spectroscopy is generally characterized by a 0 °/0 °optical geometry, which theoretically allows the collection of the specular reflected light [5]. In practice, when samples are investigated, both specular reflection (also known as surface reflection) and diffuse reflection (or volume reflection) occur, due to the roughness of the surface and to the optical properties of the material; this leads to distortions which can make the interpretation of the resulting spectra quite challenging [5, 25].

In particular the specular reflection leads to derivative-like features and inverted or reststrahlen bands, while the diffuse reflection generally leads to an improvement of weak bands intensity as compared to strong bands intensity [25].

When analysing works of art, generally both specular and diffuse reflection are present; this causes the coexistence of the above-mentioned distortions and makes it impossible to apply the Kramers-Kronig and Kubelka-Munk corrections in order to understand and interpret the spectra [5, 25].

Unfortunately, in this particular case the use of the portable FTIR was unsuccessful, as the interpretation of the obtained spectra was impossible. Indeed, the analysed fragments' paint surfaces are very irregular and rough, thus it is very likely to think that this feature caused the impossibility to understand the spectra.

Micro-sampling on the fragments was therefore necessary, in order to investigate the possible presence of organic binder with the use of transmission FTIR.

Chapter 5

Conclusions

In this case study, the characterisation of Roman mural painting fragments was attempted by means of an analytical methodology that involves both *in situ* non-destructive analysis and micro-invasive laboratory techniques. The results obtained allowed a first step towards a deeper knowledge on Roman wall paintings techniques.

The colour palette of the selected and studied wall painting fragments, showed a predominance of yellow and red paint layers, very common colours in the Roman *fresco* palette. The pigments identified were red and yellow ochre, vermilion, minium, green earth and Egyptian blue.

The investigation of the binders did not lead to any conclusions about the technique used for the fragments -*fresco* or *secco* technique-, but left new questions to be answered with future studies.

5.1 Final remarks and future outlook

As pointed out earlier, one of the main reasons of this study was to revitalise the Mora Sample Collection, a unique and valuable historical resource. It is believed that this thesis can contribute for a future renew insight into the collection.

More specifically, the totality of the fragments of wall painting contained in the collection could be studied, in order to have a complete overview of the Mora Sample Collection and its materials, from the points of view of both the material characterisation, but also from a documentation scope.

The presence within the collection of material samples already prepared to be analysed, such as cross sections embedded in resin, as well as powdered pigments, could represent a possibility for further investigation. In this case any invasive operation on the fragments would be requested, and the results could reveal important information on the materials, as well as on the reason to be of those samples.

The same methodology, already positively tested during this study, can be used to characterise the remaining fragments belonging to the Roman period for enlarging the body of knowledge about Roman mural painting techniques. Involving more specific analysis, micro-cross-sections from specific fragments, for instance, could reveal the necessary information for the characterisation of the painting technique used.

Many questions are still unanswered, mainly because of the restricted time availability for this research. For sure, whenever more studies will be undertaken, the Mora Sample Collection will be revived again.

Bibliography

[1] Gianluca Accorsi, Giovanni Verri, Margherita Bolognesi, Nicola Armaroli, Catia Clementi, Costanza Miliani, and Aldo Romani. The exceptional near-infrared luminescence properties of cuprorivaite (Egyptian blue). *Chemical Communications*, (23):3392–3394, 2009.

[2] M L Amadori, S Barcelli, G Poldi, F Ferrucci, A Andreotti, P Baraldi, and M P Colombini. Invasive and non-invasive analyses for knowledge and conservation of Roman wall paintings of the Villa of the Papyri in Herculaneum. *Microchemical Journal*, 118:183–192, 2015.

[3] R. Bacci, Mauro; Baldini, F.; Carlà, R.; and Linari. A colour analysis on the Brancacci Chapel frescoes. *In Book. Science, technology, and European cultural heritage: proceedings of the European symposium, Bologna, Italy, 13-16 June 1989*, 45(1):559–562, 1991.

[4] Edited G Berthier, M J S Dewar, H Fischer, K Fukui, H Hartmann, H H Jaffe, J Jortner, W Kutzelnigg, K Ruedenberg, E Scrocco, and W Zeil. Lecture Notes in Chemistry. In Evangelia A. Varella, editor, *Conservation Science for the Cultural Heritage*, volume 79, pages 1–13. Springer, 2013.

[5] D. Buti, F. Rosi, B. G. Brunetti, and C. Miliani. In-situ identification of copper-based green pigments on paintings and manuscripts by reflection FTIR. *Analytical and Bioanalytical Chemistry*, 405(8):2699–2711, 2013.

[6] Antonella Casoli and Sara Santoro. Organic materials in the wall paintings in Pompei: a case study of Insuladel Centenario. *Chemistry Central Journal*, 6(1):107, 2012.

[7] Tiziana Cavaleri, Annamaria Giovagnoli, and Marco Nervo. Pigments and Mixtures Identification by Visible Reflectance Spectroscopy. *Procedia Chemistry*, 8:45–54, 2013.

[8] Cennino Cennini. *Il libro dell'arte, o Trattato della pittura.* 2005.

[9] Eleni Cheilakou, Michail Troullinos, and Maria Koui. Identification of pigments on Byzantine wall paintings from Crete (14th century AD) using non-invasive Fiber Optics Diffuse Reflectance Spectroscopy (FORS). *Journal of Archaeological Science*, 41:541–555, 2014.

[10] Catia Clementi, Valeria Ciocan, Manuela Vagnini, Brenda Doherty, Marisa Laurenzi Tabasso, Cinzia Conti, Brunetto Giovanni Brunetti, and Costanza Miliani. Non-invasive and micro-destructive investigation of the Domus Aurea wall painting decorations. *Analytical and Bioanalytical Chemistry*, 401(6):1815–1826, 2011.

[11] Gaetano Corso, Monica Gelzo, Angela Chambery, Valeria Severino, Antimo Di Maro, Filomena Schiano Lomoriello, Oceania D'Apolito, Antonio Dello Russo, Patrizia Gargiulo, Ciro Piccioli, and Paolo Arcari. Characterization of pigments and ligands in a wall painting fragment from Liternum archaeological park (Italy). *Journal of Separation Science*, 35(21):2986–2993, 2012.

[12] A. Cosentino, M. Gil, M. Ribeiro, and R. Di Mauro. Technical photography for mural paintings: the newly discovered frescoes in Aci Sant'Antonio (Sicily, Italy). *Conservar Património*, 20:23–33, 2014.

[13] Antonino Cosentino. FORS spectral database of historical pigments in different binders. *e-conservation journal*, pages 53–65, 2014.

[14] B. D. Cullity. *Elements of X-RAY DIFFRACTION.* Addison-Wesley Publishing Company, Inc., 1978.

[15] Jorge Cuní. What do we know of Roman wall painting technique? Potential confounding factors in ancient paint media analysis. *Heritage Science*, 4(1):1–13, 2016.

[16] N Eastaugh, V Walsh, T Chaplin, and R Siddall. *Pigment Compendium: A Dictionary and Optical Microscopy of Historical Pigments.* Pigment Compendium: A Dictionary and Optical Microscopy of Historical Pigments. Butterworth-Heinemann, 2008.

[17] Mady Elias. The Colour of Ochres Explained by Their Composition. (February 2018), 2006.

[18] Isabel Garofano, Jose Luis Perez-Rodriguez, Maria Dolores Robador, and Adrian Duran. An innovative combination of non-invasive UVâVisible-FORS, XRD and XRF techniques to study Roman wall paintings from Seville, Spain. *Journal of Cultural Heritage*, 22:1028–1039, 2016.

[19] Monica Gelzo, Mario Grimaldi, Alessandro Vergara, Valeria Severino, Angela Chambery, Antonio Dello Russo, Ciro Piccioli, Gaetano Corso, and Paolo Arcari. Comparison of binder compositions in Pompeian wall painting styles from Insula Occidentalis. *Coke and Chemistry*, 8(1):1–10, 2014.

[20] Rutherford J. Gettens, Robert L. Feller, and W. T. Chase. Vermilion and Cinnabar. In Roy Ashok, editor, *Artists' Pigments: A Handbook of Their History and Characteristics Vol. 2*, pages 159–182.

[21] M. Gil, V. Serrão, M. L. Carvalho, S. Longelin, L. Dias, A. Cardoso, A. T. Caldeira, T. Rosado, J. Mirão, and A. E. Candeias. Material and diagnostic characterization of 17th century mural paintings by spectra-colorimetry and SEM-EDS: An insight look at José de Escovar Workshop at the CONVENT of NaSrada Saudação (Southern Portugal). *Color Research and Application*, 39(3):288–306, 2014.

[22] Carol A. Grissom. Green Earth. In Robert L. Feller, editor, *Artists' Pigments: A Handbook of Their History and Characteristics Vol. 1*, pages 141–167.

[23] Ruth Johnstone-Feller. *Colour Science in the Examination of Museum Objects.* 2001.

[24] Charlotte Martin De Fonjaudran, Austin Nevin, Francesca Piqué, and Sharon Cather. Stratigraphic analysis of organic materials in wall painting samples using

micro-FTIR attenuated total reflectance and a novel sample preparation technique. *Analytical and Bioanalytical Chemistry*, 392(1-2):77–86, 2008.

[25] C. Miliani, F. Rosi, A. Daveri, and B. G. Brunetti. Reflection infrared spectroscopy for the non-invasive in situ study of artists' pigments. *Applied Physics A: Materials Science and Processing*, 106(2):295–307, 2012.

[26] Paolo Mora, Laura Mora, and Paul Philippot. *Conservation of Wall Paintings*. Butterworth, 1984.

[27] J. W. Niemantsverdriet. *Spectroscopy in Catalysis: An Introduction: Third Edition*. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007.

[28] R. Piovesan, C. Mazzoli, L. Maritan, and P. Cornale. Fresco and lime-paint: An experimental study and objective criteria for distinguishing between these painting techniques. *Archaeometry*, 54(4):723–736, 2012.

[29] Josef Riederer. Artists' Pigments A Handbook of Their History and Characteristics Volume 3. chapter Egyptian B, pages 23–45. 1997.

[30] Manfred Schreiner, Rita Wiesinger, and Wilfried Vetter. Identification and Preservation of Cultural Heritage. *ChemViews*, (January 2018), 2017.

[31] Sebastiano Sciuti, Gabriele Fronterotta, Margherita Vendittelli, A Longoni, and C Fiornini. A Non-Destructive Analytical Study of a Recently Discovered Roman Wall Painting. *Studies in Conservation*, 46(2):132–140, 2001.

[32] Sophia Sotiropoulou, Zoi Eirini Papliaka, and Lisa Vaccari. Micro FTIR imaging for the investigation of deteriorated organic binders in wall painting stratigraphies of different techniques and periods. *Microchemical Journal*, 124:559–567, 2016.

[33] Samantha Stout, Antonino Cosentino, and Carmelo Scandurra. Non-invasive materials analysis using Portable X-ray Fluorescence (XRF). 54(6):2013, 2013.

[34] Barbara Stuart. *Analytical techniques in materials conservation*. John Wiley&Sons Ltd, The Atrium, Southern Gate, Chichester, West SussexPO198SQ,England, 2007.

[35] Diego Tamburini, Jeannette Jacqueline Lucejko, Francesca Modugno, Maria Perla Colombini, Pasquino Pallecchi, and Gianna Giachi. Microscopic techniques (LM, SEM) and a multi-analytical approach (EDX, FTIR, GC/MS, Py-GC/MS) to characterise the decoration technique of the wooden ceiling of the House of the Telephus Relief in Herculaneum (Italy). *Microchemical Journal*, 116:7–14, 2014.

[36] Theophile Theophanides. *Infrared Spectroscopy - Materials Science, Engineering and Technology*. InTech, 2012.

[37] Marco Vitruvio Pollione and Berardo Galiani. *L'Architettura di Marco Vitruvio Pollione tradotta e commentata da Berardo Galiani*. 1790.

[38] Nicoleta Vornicu, Cristina Bibire, Elena Murariu, and Daniela Ivanov. Analysis of mural paintings using in situ non-invasive XRF, FTIR spectroscopy and optical microscopy. *X-Ray Spectrometry*, 42(5):380–387, 2013.

Appendix A

The Mora Sample Collection: sites and provenance

	COUNTRY	CITY/ REGION	MONUMENT/ SITE
1	Afghanistan		
2	Algeria	Tassili	
3	Australia		
4	Austria	Gurk	
5	Belgium		
6	Colombia		
7	Croatia	Zara	
8	Czech Republic	Praga	Emmaus monastery
9	Egypt	Abu Simbel Abu Oda Luxor Saqqara Beni Hasan Gerf Hussein Qasr Ibrim Karnak Ashkelon	
10	France	Louvre	Maestro di San Sebastiano

11	Germany	Weltenburg (Bavaria)	Monastery
		Landshut (Bavaria)	
		Treviri	
12	Greece	Crete	Knossos
		Ioannina	Monastery of Filanthropinon
		Zakynthos	
13	India	Jaipur	
14	Iran	Isfahan	Chehel Sotoun
			Palace Ali Qapu
		Amol	St. Charbel Church
		Persepolis	Tachara Chateau
15	Ireland		
16	Israel	Cesarea	
		Masada	
17	Italy	Roma	Tombs under St. Peter
			Ipogeo dei Flavi
			Catacombe di Domitilla
			Palatino
			S. Ivo alla Sapienza
			Circo Diocleziano
			Casa di Livia
			Domus Aurea
			Farnesina
			Via del Pellegrino
			Pantheon
			Palazzo Farnese
			Catacomba via Salaria
			Catacomba Pretestato
			S. Clemente
		Ostia antica	
		Tarquinia	Tomba del barone

	Tomba della nave
	Tomba del cacciatore
	Tomba delle leonesse
	Tomba degli scudi
	Tomba del tifone
	Tomba degli Auguri
	Tomba di caccia e pesca
	Tomba del guerriero
Siena	
Viterbo	Cappella Mazzatosta
Velia (SA)	Temple
Torcello (VE)	
Codigoro (FE)	
Stabia (NA)	
Assisi	San Francesco (Basilica inferiore)
	San Francesco (Basilica superiore)
Agrigento	Temples
Ercolano	
Firenze	Chiostro Ognissanti
Friuli	Ragogna
Bianzano (BG)	
CittÃ Ducale (RI)	
Massafra (TA)	Cripta di S. Leonardo
Napoli	Palazzo Reale
	Catacombe S. Gennaro
Novara	Battistero
Paestum	Ninfa
Orvieto	Cappella Santa Brizia
Pisa	Camposanto
Padova	Cappella degli Scrovegni
	Cappella Ovetari
Pompei	Casa del Larario

		Pomposa (FE)	
		Santa Maria di Cerrate (LE)	
18	Japan		
19	Libia	Tadrart	
20	Malta	Mdina	SS. Pietro e Paolo
		Gozo	
21	Mexico	Mexico City	Tlatelolco
22	Morocco	Rabat	
23	Nepal	Kathmandu	
24	Oman		
25	Peru	Lima	
26	Portugal	Belmonte	Igreja de Santiago
27	Romania	Sucevita	
		Gura Humor	
		Voronet	
28	Serbia	Ravanica	Monastery
29	Spain	Segovia	
30	Sri Lanka	Ceylon	
31	Switzerland	Neuchatel	
		Geneve	Chateau de Genthod
32	Thailand	Wat Yai Intharam Chonburi	
		Wat Yai Suwannaram Phetchaburi	
		Wat Ratchaburana Ayutthaia	
33	Tunisia	Tunisi (?)	
		Bassins des Aghlabides (?)	
34	Turkey	Gorenez Dagi	
		Catalhuyuk	
		Goreme	Carikli Kilise
			Elmali Kilise
35	United Kingdom		

Appendix B

Fragments description

In the following table the description of the considered 56 fragments and information about their provenance are reported.

The 15 fragments selected for micro-sampling and analysed by means of μ-FTIR are highlighted.

FRAGMENT REFERENCE	PROVENANCE (box/label reference)	PROVENANCE (catalogue reference)	PAINT LAYER VISUAL COLOUR
B2F1	43 VARANO	VITERBO	Green
B2F2	43 VARANO	VITERBO	Blue
B2F3	43 VARANO	VITERBO	Yellow
B2F6	92 TARQUINIA	Tarquinia 92 ; ITALIA 2 a,b,c	Red
B2F10	VELIA 129 TEMPIO V sec; 121 sezioni affreschi	129 VELIA-Tempio V sec.	Red
B2F11	VELIA 129 TEMPIO V sec; 121 sezioni affreschi	130 VELIA-Tempio V sec.	Yellow
B2F15	VELIA 129 TEMPIO V sec; 121 sezioni affreschi	131 VELIA-Tempio V sec.	Red
B2F12	VITERBO 28 MAZZATOSTA	VITERBO 28 MAZZATOSTA	Blue
B4F4	TERZO STILE "SCAVI DI POMPEI"	Verde rosa (rosso) – III Stile ?	Red, yellow, green, pink
B4F8	SECONDO STILE "SCAVI DI POMPEI"	Pompei Secondo Stile	Red, green
B4F9	Roma Pompei sezioni e prove; ROMA – POMPEI 111 SEZIONI E PROVE	111 Roma – Pompei – sezioni e prove	Red, yellow, black
B4F13	Pomposa refettorio	?	Green
B5F2	Intonaci Romani Palatino ?	Roma Palatino - Rossi	Red, yellow, green
B5F4	Intonaci Romani Palatino ?	Roma Palatino - Rossi	Red, yellow, white
B5F5	Intonaci Romani Palatino ?	Roma Palatino - Rossi	Red, blue, green, brown
B5F7	Intonaci Romani Palatino ?	Roma Palatino - Rossi	Red, grey
B5F8	Intonaci Romani Palatino ?	Roma Palatino - Rossi	Red, yellow, green, black
B5F9	Intonaci Romani Palatino ?	Roma Palatino - Rossi	Red, pink, black
B5F10	Intonaci Romani Palatino ?	Roma Palatino - Rossi	Red, white
B5F12	Intonaci Romani Palatino ?	Roma Palatino - Rossi	Red
B5F13	Intonaci Romani Palatino ?	Roma Palatino - Rossi	Red, yellow
B5F16	Intonaci Romani Palatino ?	Roma Palatino - Rossi	Red, yellow
B5F22	Intonaci Romani Palatino ?	Roma Palatino - Rossi	Red
B6F1	B3 PALATINO NUOVI SCAVI 28.V.1969	B.3 Palatino – Nuovi scavi 28.V.69	Blue
B6F13	θ 6	θ6 ; Italy?	Red, green
B6F14	45 VARI ; 135 FRAMMENTI VARI ROMA	Frammenti vari 135 Roma	Red, green, yellow
B6F16	45 VARI ; 135 FRAMMENTI VARI ROMA	Frammenti vari 135 Roma	Blue
B6F17	45 VARI ; 135 FRAMMENTI VARI ROMA	Frammenti vari 135 Roma	Blue
B6F19	-	?	Red
B7F4	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Blue, red
B7F9	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Blue, yellow

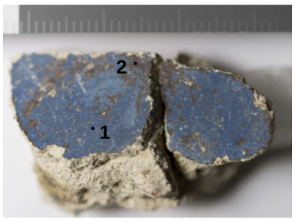
B7F11	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Pink
B7F21	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Green, red
B7F23	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Green
B7F24	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Blue
B7F28	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Green, red, yellow
B7F29	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Red, pink, black
B7F32	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Red
B7F46	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Yellow
B7F47	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Orange
B7F48	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Blue
B7F50	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Green
B7F51	Palatino – Roma Vari 45 - vicino casa di Livia	Palatino – Roma vari 45 – Close to Casa di Livia	Green
B8F1	Catacombe Domitilla - Cappella di Ampliato (CAT DOM 143)	Domitilla ɣa ; ITALIA 50	Green, red, white
B8F3	Catacomba Domitilla - Cappella di Ampliato (CAT DOM 143)	Catacombe Domitilla	Green, red, white
B9F1	15 Tarquinia – Tori ; Tomba dei Tori - Tarquinia	15 Tarquinia-TORI-"Tori" Tomb in Tarquinia	Green, red, yellow
B11F1	Catacombe	?	Green, red
B13F1	113 ROMA – Roma terra riporto Colle Appio Frammento con zampe di cavallo	Terra di riporto Colle Oppio - Frammento con zampe di cavallo ; Italia 6 ; ?	Red
B13F2	113 ROMA – Roma terra riporto Colle Appio Frammento con zampe di cavallo	Roma 113 Italia 6	Black, green
B13F3	Frammenti non identificati Roma?	Frammenti non identificati – Roma? Italia 6 ; ?	Red
B13F4	Roma scarico (?) Tecnica pittorica	-	Blue
B13F6	Roma scarico (?) Tecnica pittorica	-	Red, yellow
B13F11	Roma scarico (?)	ROMA srair (? Illeggibile) ; Italia 6	Red, yellow
B13F12	Roma scarico (?)	ROMA srair (? Illeggibile) ; Italia 6	Red
B18F1	Egypt	-	Blue
B18F2	Egypt	-	Blue

Appendix C

Analysis indications

The 56 fragments' overviews are shown below with the colorimetric, spectrophotometric and elemental analysis locations indicated.

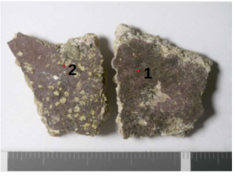
B2F1



B2F2

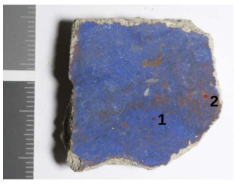
B2F3

B2F6



B2F10

B2F11



B2F12

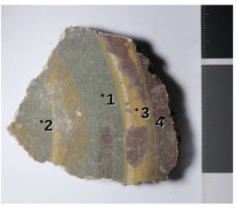
B2F15


B4F4


B4F8

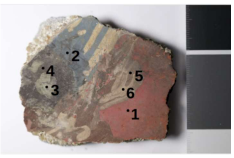

B4F9


B4F13



B5F2

B5F4



B5F5

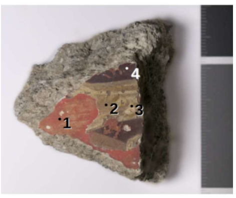
B5F7

B5F8

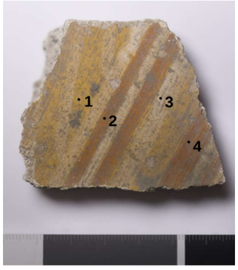
B5F9

B5F10

B5F12



B5F13



B5F16

B5F22

B6F1

B6F13

B6F14

B6F16

B6F17

B6F19

B7F4

B7F9

B7F11

B7F21

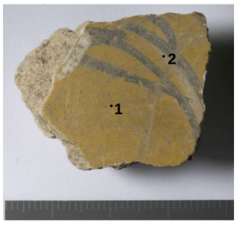
B7F23

B7F24

B7F28

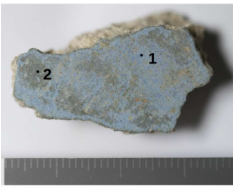
B7F29

B7F32



B7F46

B7F47

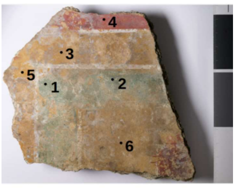


B7F49

B7F50-51

B8F1

B8F3



B9F1

B11F1

B13F1

B13F2

B13F2

B13F3

B13F4

B13F6

B13F11

B13F12

B18F1

B18F2

Appendix D

EDXRF elemental analysis results

The elemental analysis results concerning the red paint layers containing iron (Fe) are reported in the following table.

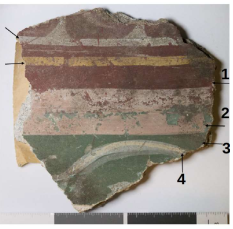
Table D.1: EDXRF results of red Fe-containing samples.

												Element
Line	B4F4-3	B4F8-1	B5F2-4	B6F14-1	B7F28-3	B8F1-1	B8F3-1	B13F1-1	B13F1-2	B13F6-2	B13F12-1	
Si	K12	0,147	0,158	0,294	0,142	0,273	0,295	0,271	0,171	0,136	0,136	0,165
S	K12	0,364	1,845	0,376	0,346	0,089	0,061	0,104	0,152	0,136	0,202	0,068
Ca	K12	54,537	70,387	60,770	58,036	83,153	82,151	78,393	68,679	70,004	65,686	61,739
Ti	K12	0,312	0,293	0,460	0,419	0,148	0,353	0,530	0,340	0,325	0,325	0,373
V	K12	0,000	0,108	0,021	0,000	0,000	0,046	0,179	0,013	0,008	0,016	0,000
Cr	K12	0,041	0,014	0,056	0,045	0,281	0,005	0,008	0,014	0,048	0,023	0,026
Mn	K12	0,423	0,532	0,560	1,695	0,149	0,171	1,664	0,272	0,312	0,586	0,788
Fe	K12	89,967	64,617	73,252	132,078	34,937	41,438	44,679	47,618	49,282	122,439	110,662
Ni	K12	1,472	1,610	1,459	1,406	2,125	1,849	1,831	1,694	1,694	1,448	1,340
Cu	K12	0,154	0,112	0,296	0,739	0,169	0,306	0,137	0,142	0,148	0,189	0,318
Zn	K12	0,100	0,435	0,073	0,306	0,046	0,153	0,140	0,205	0,151	0,618	0,131
As	K12	3,130	2,142	2,420	2,178	1,415	1,362	1,120	0,749	0,827	2,585	1,902
Sr	K12	0,565	1,644	1,793	4,994	2,559	1,519	1,566	4,052	4,712	6,270	1,615
Rh	K12	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Rh	L1	2,006	1,385	1,462	1,942	1,278	1,525	1,326	1,881	1,865	1,732	1,705
Ac	L1	0,878	1,075	0,439	1,594	0,256	0,273	0,314	0,262	0,322	1,905	1,358
Ac	M1	0,906	0,471	0,744	0,511	0,774	0,804	0,603	0,799	0,778	0,539	0,526

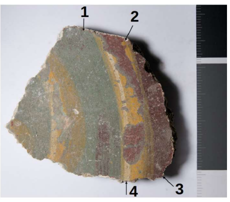
Appendix E

μ-sampling

The 15 fragments' overviews with indication of the micro-sampling locations are shown below.



B4F4

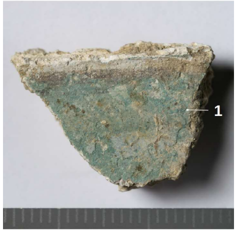


B5F2

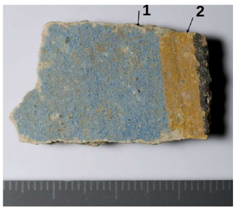
B5F5

B6F1

B6F16



B6F17



B7F9

B7F11

B7F21	B7F23	B7F28	B7F47
			
B7F48	B7F51	B13F1	

Appendix F

μ-FTIR results

In the following table the micro-FTIR results of the 28 micro-samples are reported.

Sample reference	Colour	Identified materials
B4F4-1	Red	Kaolinite + Goethite + Calcite + Gypsum (traces)
B4F4-2	Pink	Kaolinite (traces) + Celadonite (traces) + Gypsum + Dolomite + Calcite + Aragonite
B4F4-3	Green	Celadonite + Calcite + Gypsum (traces)
B4F4-4	White	Gypsum + Dolomite + Calcite + Aragonite
B5F2-1	Green	Celadonite + Egyptian blue + Gypsum + Kaolinite (traces) + Quartz + Calcite + oxalates
B5F2-2	Yellow	Kaolinite + Gypsum + Dolomite + Calcite
B5F2-3	Red	Kaolinite + Gypsum (traces) + Dolomite + Calcite + Aragonite
B5F2-4	White	Kaolinite + Goethite + Gypsum + Dolomite + Calcite
B5F5-1	Black	Celadonite + Kaolinite + Quartz + Gypsum + Dolomite + Calcite
B5F5-2	White	Kaolinite + Gypsum + Dolomite + Calcite
B5F5-3	Brown	Egyptian blue + Kaolinite (traces) + Gypsum + Dolomite + Calcite + Aragonite
B5F5-4	Red	Kaolinite + Goethite + Gypsum + Calcite + Aragonite
B6F1	Blue	Egyptian blue + Dolomite + Calcite

B6F16	Blue	Egyptian blue + Calcite
B6F17	Green	Celadonite + Egyptian blue + Gypsum + Calcite
B7F9-1	Blue	Egyptian blue + Celadonite + Calcite + Aragonite
B7F9-2	Yellow	Kaolinite + Goethite + Gypsum + Dolomite + Calcite + Aragonite
B7F11	Pink	Egyptian blue + Dolomite + Calcite + Inorganic compound
B7F21	Green	Celadonite + Calcite + Aragonite
B7F23	Green	Celadonite + Egyptian blue + Kaolinite (traces) + Gypsum + Calcite
B7F28-1	Green	Celadonite + Kaolinite (traces) + Dolomite + Calcite + Aragonite
B7F28-2	Red	Kaolinite + Gypsum (traces) + Calcite
B7F47	Orange	Calcite
B7F48	Blue	Egyptian blue + Celadonite + Kaolinite (traces) + Calcite + Aragonite
B7F51-1	Black	Kaolinite (traces) + Calcite
B7F51-2	Green	Celadonite + Calcite
B13F1-1	White	Kaolinite + Gypsum (traces) + Dolomite + Calcite + Aragonite
B13F1-2	Red	Kaolinite + Gypsum + Calcite

EXAM WORKSHEET

PROJECT THE MORA SAMPLE COLLECTION REORGANIZATION AND DESCRIPTION

GENERAL DATA
Site/object: Pompeii
Country: Italy
City: Naples
Typology: mural painting
Chronological period: Roman
Painting location: unknown

SPECIFIC DATA
Sample ID: B4F4
Description: decorative paint layer with overlapping paint layers
EXAMS
Exams: OM-Vis; colorimetry and spectrophotometry; FORS; EDXRF
Aim:
a) Register paint surface texture and details
b) First pigment characterisation
Date of the exams: March-April 2018
Responsible: Milene Gil
Executant: Cecilia Laurita

Equipment and experimental conditions:
Details of pigments particles (stable and altered within the paint layers were observed and recorded with two types of hand-held optical digital microscopes *Dinolite Premier* AD3713TB and *Dinolite* PRO AM413T-FVW working in visible inputs at 20x and 430x magnifications.
Colorimetric data were collected in all matte surface with a DataColor CheckPlusII (Lawrenceville, NJ), equipped with an integrating sphere in the following conditions: diffuse illumination 8° viewing (in agreement with the CIE publication No.15.2.Colorimetry), SCE and standard Illuminant/Observer D65/10°. The aperture size was UXAV (Ø 2.5 mm) due to small color details. The results obtained in the CIE *L*a*b** chromatic space, defined by the International Commission on Illumination (CIE) in 1976, are the average of three measurements. The chromatic coordinates measured were *L** (lightness 0-100), *a** (red/green axes 0-100) and *b** (yellow/blue hue axes 0-100).
Fiber Optics Reflectance Spectroscopy (FORS) was performed with a LR1-compact spectrometer (*aseq. intruments*, Canada) with a Toshiba TCD 1304DG linear array detector in the range of 300-1000 nm with a spectral resolution <1 nm (with 50 µm slit). Other specifications: A/D resolution 14bit; signal to noise ratio 300:1, exposure time 2.5ms-10s, CCD reading time 14m. A Fiber optMA905 to 0.22 numerical aperture single-strand optical fiber was used for the measurements and the results were treated in Lab View software.
Elemental analysis were carried out through Energy Dispersive X-Ray Fluorescence (EDXRF), using a portable Bruker Tracer III-SD spectrometer, equipped with a Rh excitation source and an X-Flash® SDD detector. The measurements were made without any filters and obtained with 40 kV high voltage, a current of 30µA and an acquisition time of 60s.

RESULTS

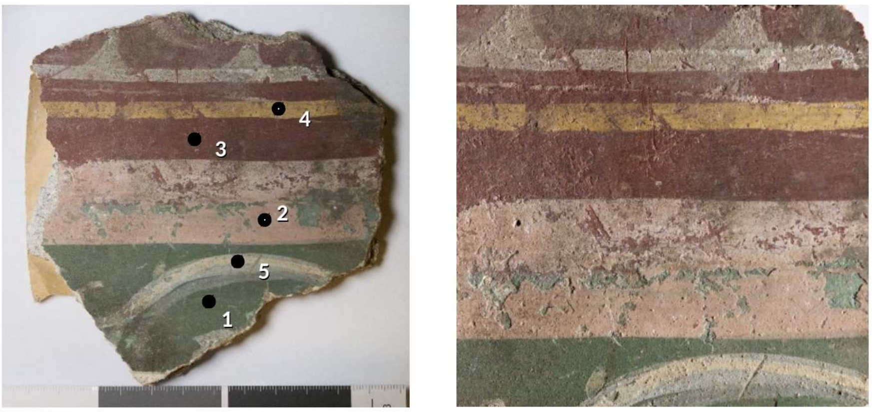


Fig. 1 a/b: sample overview (front) with indication of colorimetric and spectrophotometry spot analysis; detail of paint layers in Vis-Rak

POINT	COLOUR	MAGNIFICATION	PHOTO REF.	COLORIMETRIC REF.
1	Green	50x	Frag4_1_50x	b4f4-1
		435x	Frag4_1_435x	
2	Pink	50x	Frag4_2_50x	b4f4-2
		435x	Frag4_2_435xa, b	
3	Red	50x	Frag4_3_50x	b4f4-3
		435x	Frag4_3_435x	
4	Yellow	50x	Frag4_4_50x	b4f4-4
		435x	Frag4_4_435x	
5	White	50x	Frag4_5_50x	b4f4-5
		435x	Frag4_5_435x	
6	White + blue	50x	Frag4_6_50x	
		435x	Frag4_6_435x	

Table 1: spot analysis description

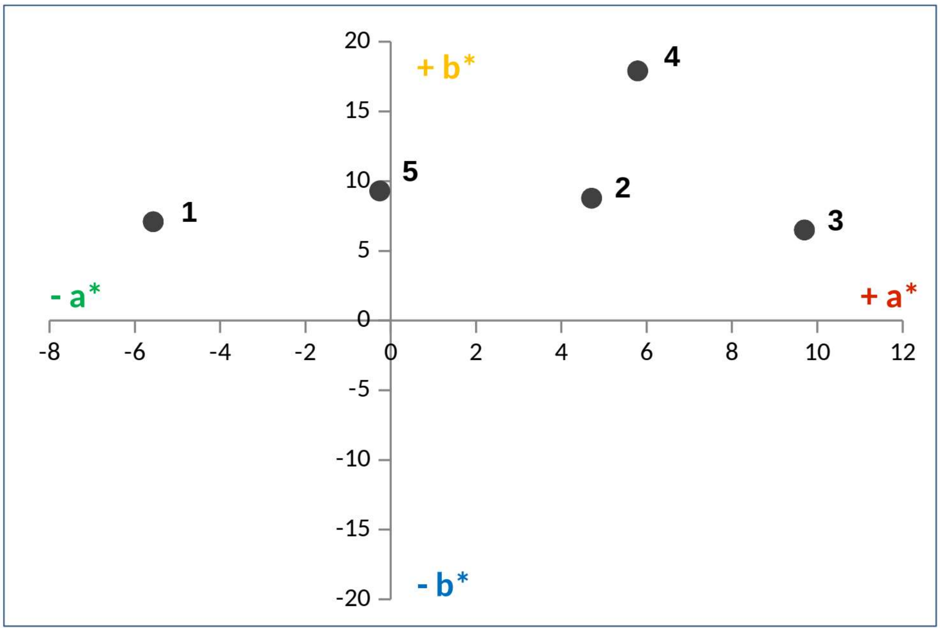


Fig. 2: global view of the 5 paint layers analysed in the bidimensional CIEa*b* colour space

ICCROM

EXAM WORKSHEET

PROJECT THE MORA SAMPLE COLLECTION REORGANIZATION AND DESCRIPTION

GENERAL DATA
Site/object: Pompeii
Country: Italy
City: Naples
Typology: mural painting
Chronological period: Roman
Painting location: unknown

SPECIFIC DATA
Sample ID: B4F4
Description: decorative paint layer with overlapping paint layers
EXAMS
Exams: OM-Vis; colorimetry and spectrophotometry; FORS; EDXRF
Aim:
a) Register paint surface texture and details
b) First pigment characterisation
Date of the exams: March-April 2018
Responsible: Milene Gil
Executant: Cecilia Laurita

Equipment and experimental conditions:
Details of pigments particles (stable and altered within the paint layers were observed and recorded with two types of hand-held optical digital microscopes *Dinolite Premier* AD3713TB and *Dinolite* PRO AM413T-FVW working in visible inputs at 20x and 430x magnifications.
Colorimetric data were collected in all matte surface with a DataColor CheckPlusII (Lawrenceville, NJ), equipped with an integrating sphere in the following conditions: diffuse illumination 8° viewing (in agreement with the CIE publication No.15.2.Colorimetry), SCE and standard Illuminant/Observer D65/10°. The aperture size was UXAV (Ø 2.5 mm) due to small color details. The results obtained in the CIE *L*a*b** chromatic space, defined by the International Commission on Illumination (CIE) in 1976, are the average of three measurements. The chromatic coordinates measured were *L** (lightness 0-100), *a** (red/green axes 0-100) and *b** (yellow/blue hue axes 0-100).
Fiber Optics Reflectance Spectroscopy (FORS) was performed with a LR1-compact spectrometer (*aseq. intruments*, Canada) with a Toshiba TCD 1304DG linear array detector in the range of 300-1000 nm with a spectral resolution <1 nm (with 50 μm slit). Other specifications: A/D resolution 14bit; signal to noise ratio 300:1, exposure time 2.5ms-10s, CCD reading time 14m. A Fiber optMA905 to 0.22 numerical aperture single-strand optical fiber was used for the measurements and the results were treated in Lab View software.
Elemental analysis were carried out through Energy Dispersive X-Ray Fluorescence (EDXRF), using a portable Bruker Tracer III-SD spectrometer, equipped with a Rh excitation source and an X-Flash® SDD detector. The measurements were made without any filters and obtained with 40 kV high voltage, a current of 30μA and an acquisition time of 60s.

RESULTS

Fig. 3: sample overview (front) with indication of colorimetric and spectrophotometric analysis of spot 1

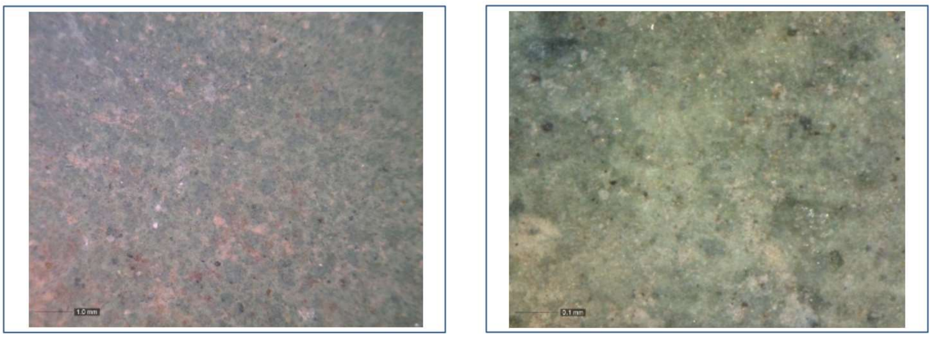


Fig. 4 a/b: spot 1 - OM in Vis (60x and 435x)

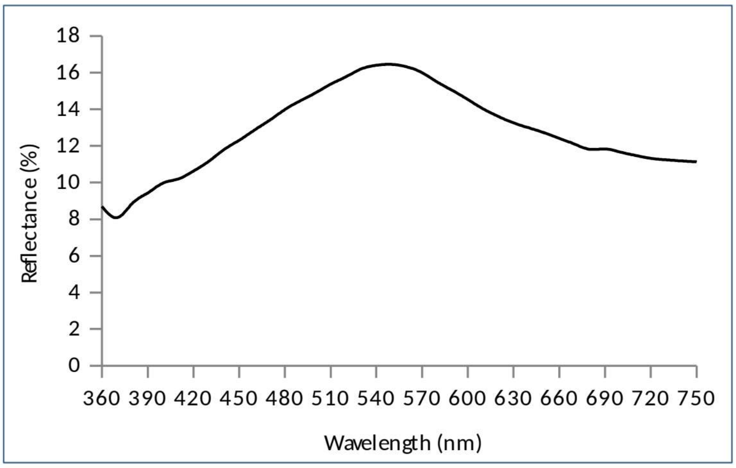


Fig. 5: diffuse reflectance spectral curve (360-750 nm)

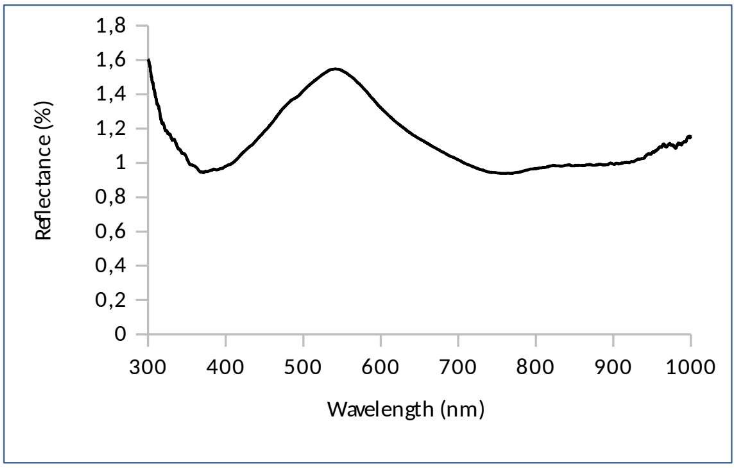


Fig. 6: reflectance spectral curve (300-1000 nm)

Observations/discussion:

Due to the high amount of iron (Fe) and calcium (Ca), the green pigment can be associated to green earth. The diffuse reflectance curve can confirm the hypothesis, since it presents the two reflectance maxima at 560 and 810nm characteristic of green earth.

EXAM WORKSHEET

PROJECT THE MORA SAMPLE COLLECTION REORGANIZATION AND DESCRIPTION

GENERAL DATA
Site/object: Pompeii
Country: Italy
City: Naples
Typology: mural painting
Chronological period: Roman
Painting location: unknown

SPECIFIC DATA
Sample ID: B4F4
Description: decorative paint layer with overlapping paint layers
EXAMS
Exams: OM-Vis; colorimetry and spectrophotometry; FORS; EDXRF
Aim:
a) Register paint surface texture and details
b) First pigment characterisation
Date of the exams: March-April 2018
Responsible: Milene Gil
Executant: Cecilia Laurita

Equipment and experimental conditions:
Details of pigments particles (stable and altered within the paint layers were observed and recorded with two types of hand-held optical digital microscopes *Dinolite Premier* AD3713TB and *Dinolite* PRO AM413T-FVW working in visible inputs at 20x and 430x magnifications.
Colorimetric data were collected in all matte surface with a DataColor CheckPlusII (Lawrenceville, NJ), equipped with an integrating sphere in the following conditions: diffuse illumination 8° viewing (in agreement with the CIE publication No.15.2.Colorimetry), SCE and standard Illuminant/Observer D65/10°. The aperture size was UXAV (Ø 2.5 mm) due to small color details. The results obtained in the CIE *L*a*b** chromatic space, defined by the International Commission on Illumination (CIE) in 1976, are the average of three measurements. The chromatic coordinates measured were *L** (lightness 0-100), *a** (red/green axes 0-100) and *b** (yellow/blue hue axes 0-100).
Fiber Optics Reflectance Spectroscopy (FORS) was performed with a LR1-compact spectrometer (*aseq. intruments*, Canada) with a Toshiba TCD 1304DG linear array detector in the range of 300-1000 nm with a spectral resolution <1 nm (with 50 µm slit). Other specifications: A/D resolution 14bit; signal to noise ratio 300:1, exposure time 2.5ms-10s, CCD reading time 14m. A Fiber optMA905 to 0.22 numerical aperture single-strand optical fiber was used for the measurements and the results were treated in Lab View software.
Elemental analysis were carried out through Energy Dispersive X-Ray Fluorescence (EDXRF), using a portable Bruker Tracer III-SD spectrometer, equipped with a Rh excitation source and an X-Flash® SDD detector. The measurements were made without any filters and obtained with 40 kV high voltage, a current of 30µA and an acquisition time of 60s.

RESULTS

Fig. 7: sample overview (front) with indication of colorimetric and spectrophotometric analysis of spot 2

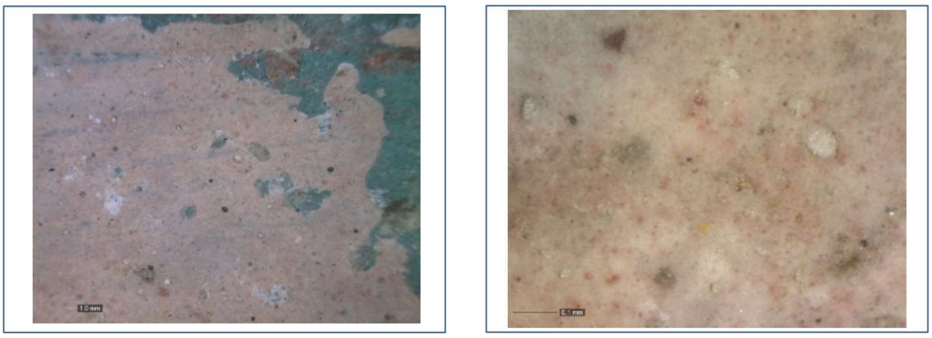


Fig. 8 a/b: spot 2 - OM in Vis (60x and 430x)

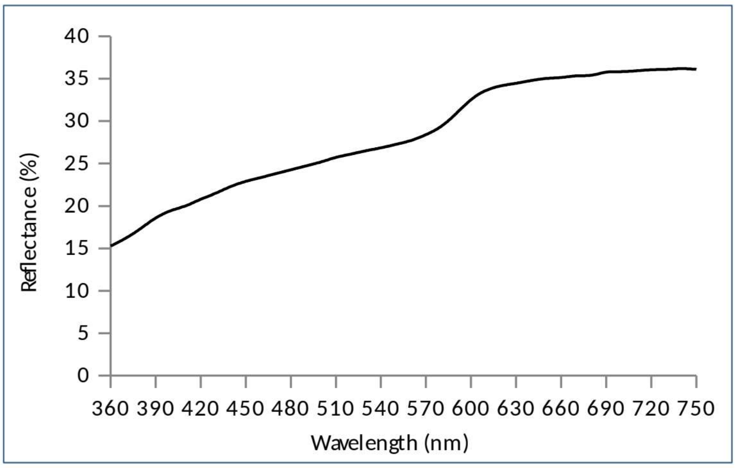


Fig. 9: diffuse reflectance spectral curve (360-750 nm)

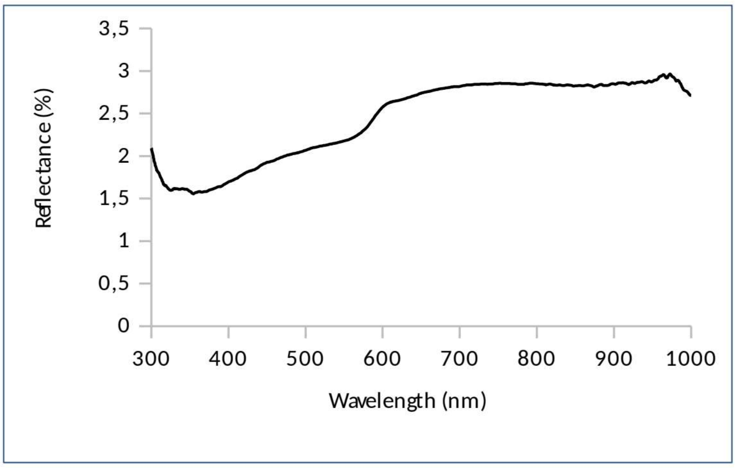


Fig. 10: reflectance spectral curve (300-1000 nm)

Observations/discussion:

EXAM WORKSHEET

PROJECT THE MORA SAMPLE COLLECTION REORGANIZATION AND DESCRIPTION

GENERAL DATA
Site/object: Pompeii
Country: Italy
City: Naples
Typology: mural painting
Chronological period: Roman
Painting location: unknown

SPECIFIC DATA
Sample ID: B4F4
Description: decorative paint layer with overlapping paint layers
EXAMS
Exams: OM-Vis; colorimetry and spectrophotometry; FORS; EDXRF
Aim:
a) Register paint surface texture and details
b) First pigment characterisation
Date of the exams: March-April 2018
Responsible: Milene Gil
Executant: Cecilia Laurita

Equipment and experimental conditions:
Details of pigments particles (stable and altered within the paint layers were observed and recorded with two types of hand-held optical digital microscopes *Dinolite Premier* AD3713TB and *Dinolite* PRO AM413T-FVW working in visible inputs at 20x and 430x magnifications.
Colorimetric data were collected in all matte surface with a DataColor CheckPlusII (Lawrenceville, NJ), equipped with an integrating sphere in the following conditions: diffuse illumination 8° viewing (in agreement with the CIE publication No.15.2.Colorimetry), SCE and standard Illuminant/Observer D65/10°. The aperture size was UXAV (Ø 2.5 mm) due to small color details. The results obtained in the CIE *L*a*b** chromatic space, defined by the International Commission on Illumination (CIE) in 1976, are the average of three measurements. The chromatic coordinates measured were *L** (lightness 0-100), *a** (red/green axes 0-100) and *b** (yellow/blue hue axes 0-100).
Fiber Optics Reflectance Spectroscopy (FORS) was performed with a LR1-compact spectrometer (*aseq. intruments*, Canada) with a Toshiba TCD 1304DG linear array detector in the range of 300-1000 nm with a spectral resolution <1 nm (with 50 µm slit). Other specifications: A/D resolution 14bit; signal to noise ratio 300:1, exposure time 2.5ms-10s, CCD reading time 14m. A Fiber optMA905 to 0.22 numerical aperture single-strand optical fiber was used for the measurements and the results were treated in Lab View software.
Elemental analysis were carried out through Energy Dispersive X-Ray Fluorescence (EDXRF), using a portable Bruker Tracer III-SD spectrometer, equipped with a Rh excitation source and an X-Flash® SDD detector. The measurements were made without any filters and obtained with 40 kV high voltage, a current of 30µA and an acquisition time of 60s.

RESULTS

Fig. 11: sample overview (front) with indication of colorimetric and spectrophotometric analysis of spot 3

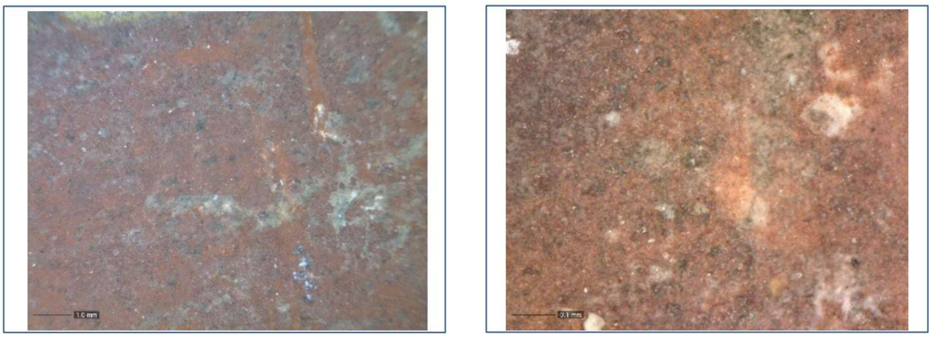


Fig. 12 a/b: spot 3 - OM in Vis (60x and 435x)

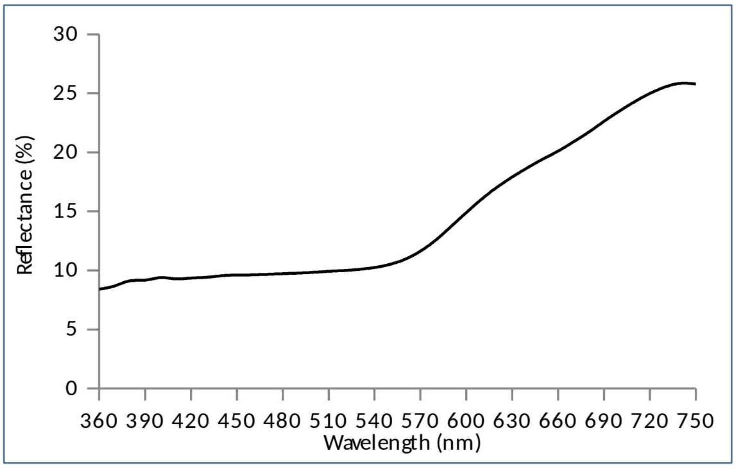


Fig. 13: diffuse reflectance spectral curve (360-750 nm)

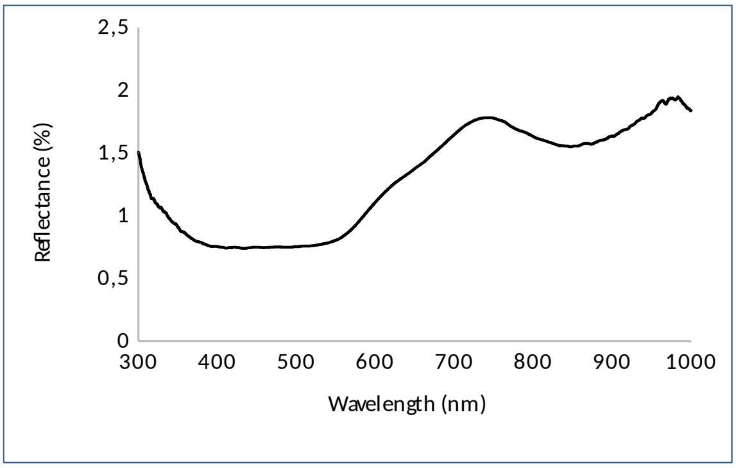


Fig. 14: reflectance spectral curve (300-1000 nm)

Observations/discussion:

The EDXRF elemental analysis reveals a high amount of iron (Fe) and calcium (Ca) that can be referred to a red ochre pigment.

ICCROM

EXAM WORKSHEET

PROJECT THE MORA SAMPLE COLLECTION REORGANIZATION AND DESCRIPTION

GENERAL DATA
Site/object: Pompeii
Country: Italy
City: Naples
Typology: mural painting
Chronological period: Roman
Painting location: unknown

SPECIFIC DATA
Sample ID: B4F4
Description: decorative paint layer with overlapping paint layers
EXAMS
Exams: OM-Vis; colorimetry and spectrophotometry; FORS; EDXRF
Aim:
a) Register paint surface texture and details
b) First pigment characterisation
Date of the exams: March-April 2018
Responsible: Milene Gil
Executant: Cecilia Laurita

Equipment and experimental conditions:

Details of pigments particles (stable and altered within the paint layers were observed and recorded with two types of hand-held optical digital microscopes *Dinolite Premier* AD3713TB and *Dinolite* PRO AM413T-FVW working in visible inputs at 20x and 430x magnifications.

Colorimetric data were collected in all matte surface with a DataColor CheckPlusII (Lawrenceville, NJ), equipped with an integrating sphere in the following conditions: diffuse illumination 8° viewing (in agreement with the CIE publication No.15.2.Colorimetry), SCE and standard Illuminant/Observer D65/10°. The aperture size was UXAV (Ø 2.5 mm) due to small color details. The results obtained in the CIE *L*a*b** chromatic space, defined by the International Commission on Illumination (CIE) in 1976, are the average of three measurements. The chromatic coordinates measured were *L** (lightness 0-100), *a** (red/green axes 0-100) and *b** (yellow/blue hue axes 0-100).

Fiber Optics Reflectance Spectroscopy (FORS) was performed with a LR1-compact spectrometer (*aseq. intruments*, Canada) with a Toshiba TCD 1304DG linear array detector in the range of 300-1000 nm with a spectral resolution <1 nm (with 50 μm slit). Other specifications: A/D resolution 14bit; signal to noise ratio 300:1, exposure time 2.5ms-10s, CCD reading time 14m. A Fiber optMA905 to 0.22 numerical aperture single-strand optical fiber was used for the measurements and the results were treated in Lab View software.

Elemental analysis were carried out through Energy Dispersive X-Ray Fluorescence (EDXRF), using a portable Bruker Tracer III-SD spectrometer, equipped with a Rh excitation source and an X-Flash® SDD detector. The measurements were made without any filters and obtained with 40 kV high voltage, a current of 30μA and an acquisition time of 60s.

RESULTS

Fig. 15: sample overview (front) with indication of colorimetric and spectrophotometric analysis of spot 4

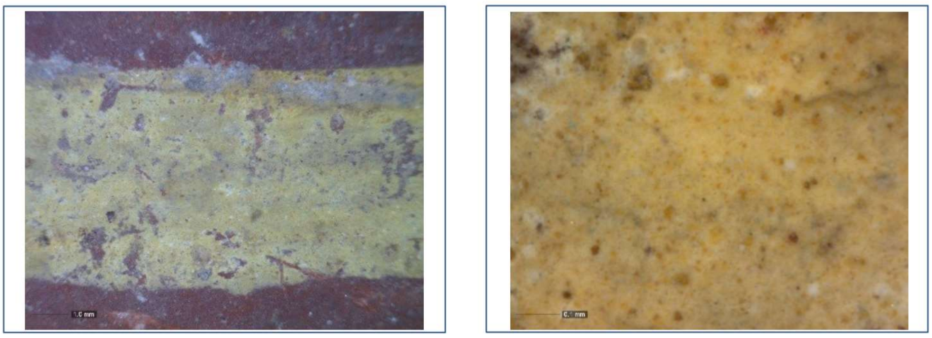


Fig. 16 a/b: spot 4 - OM in Vis (60x and 435x)

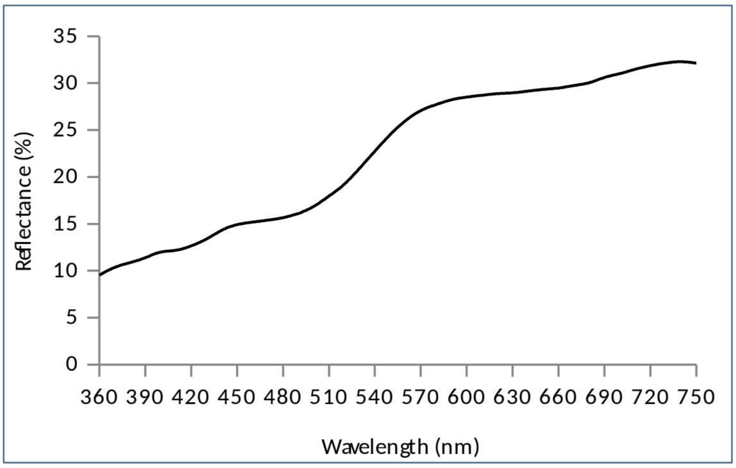


Fig. 17: diffuse reflectance spectral curve (360-750 nm)

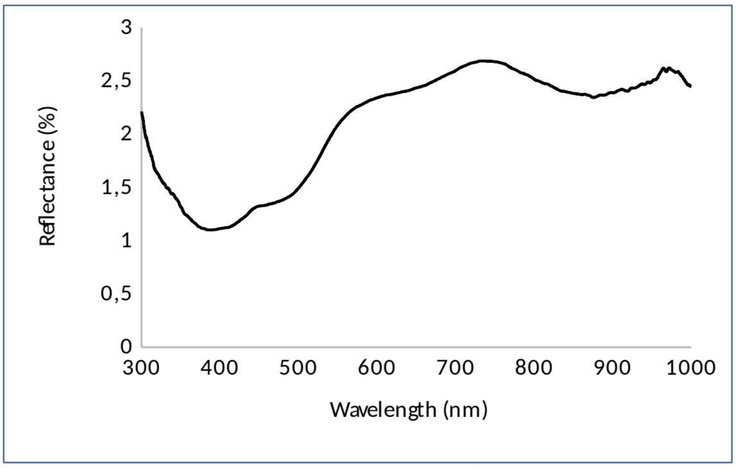


Fig. 18: reflectance spectral curve (300-1000 nm)

Observations/discussion:

The EDXRF elemental analysis revealed a high amount of iron (Fe) and calcium (Ca), suggesting the presence of yellow ochre. The diffuse reflectance spectral curve shows the s-shape with abs bands at 660 and 930 nm, typical of this pigment.

EXAM WORKSHEET

PROJECT THE MORA SAMPLE COLLECTION REORGANIZATION AND DESCRIPTION

GENERAL DATA
Site/object: Pompeii
Country: Italy
City: Naples
Typology: mural painting
Chronological period: Roman
Painting location: unknown

SPECIFIC DATA
Sample ID: B4F4
Description: decorative paint layer with overlapping paint layers
EXAMS
Exams: OM-Vis; colorimetry and spectrophotometry; FORS; EDXRF
Aim:
a) Register paint surface texture and details
b) First pigment characterisation
Date of the exams: March-April 2018
Responsible: Milene Gil
Executant: Cecilia Laurita

Equipment and experimental conditions:
Details of pigments particles (stable and altered within the paint layers were observed and recorded with two types of hand-held optical digital microscopes *Dinolite Premier* AD3713TB and *Dinolit*e PRO AM413T-FVW working in visible inputs at 20x and 430x magnifications.

Colorimetric data were collected in all matte surface with a DataColor CheckPlusII (Lawrenceville, NJ), equipped with an integrating sphere in the following conditions: diffuse illumination 8° viewing (in agreement with the CIE publication No.15.2.Colorimetry), SCE and standard Illuminant/Observer D65/10°. The aperture size was UXAV (Ø 2.5 mm) due to small color details. The results obtained in the CIE *L*a*b** chromatic space, defined by the International Commission on Illumination (CIE) in 1976, are the average of three measurements. The chromatic coordinates measured were *L** (lightness 0-100), *a** (red/green axes 0-100) and *b** (yellow/blue hue axes 0-100).

Fiber Optics Reflectance Spectroscopy (FORS) was performed with a LR1-compact spectrometer (*aseq. intruments*, Canada) with a Toshiba TCD 1304DG linear array detector in the range of 300-1000 nm with a spectral resolution <1 nm (with 50 µm slit). Other specifications: A/D resolution 14bit; signal to noise ratio 300:1, exposure time 2.5ms-10s, CCD reading time 14m. A Fiber optMA905 to 0.22 numerical aperture single-strand optical fiber was used for the measurements and the results were treated in Lab View software.

Elemental analysis were carried out through Energy Dispersive X-Ray Fluorescence (EDXRF), using a portable Bruker Tracer III-SD spectrometer, equipped with a Rh excitation source and an X-Flash® SDD detector. The measurements were made without any filters and obtained with 40 kV high voltage, a current of 30µA and an acquisition time of 60s.

RESULTS

Fig. 19: sample overview (front) with indication of colorimetric and spectrophotometric analysis of spot 5

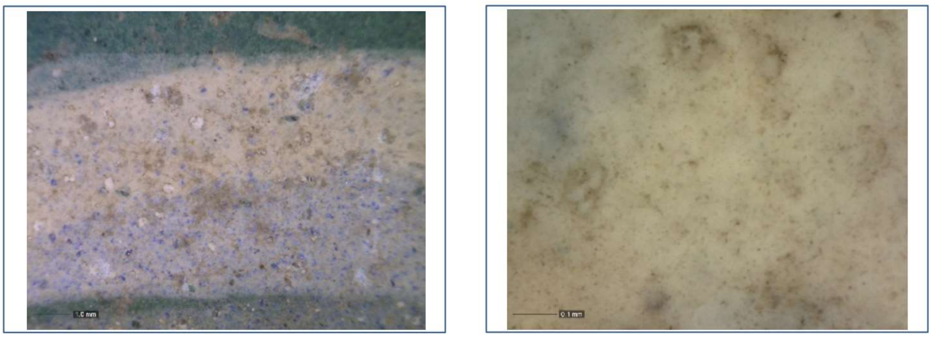


Fig. 20 a/b: spot 5 - OM in Vis (60x and 435x)

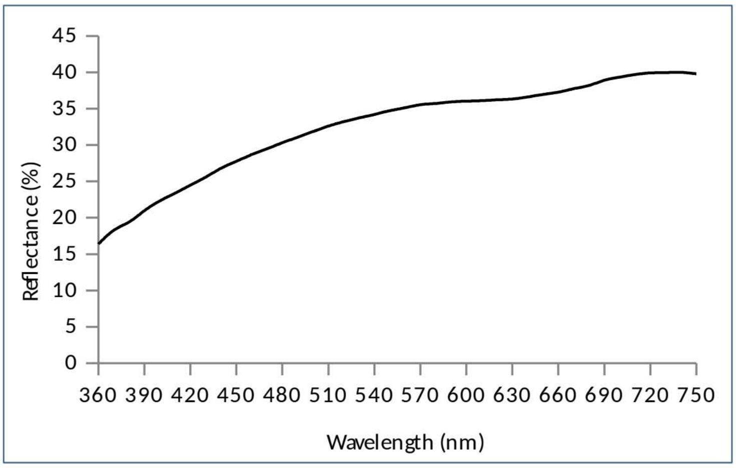


Fig. 21: diffuse reflectance spectral curve (360-750 nm)

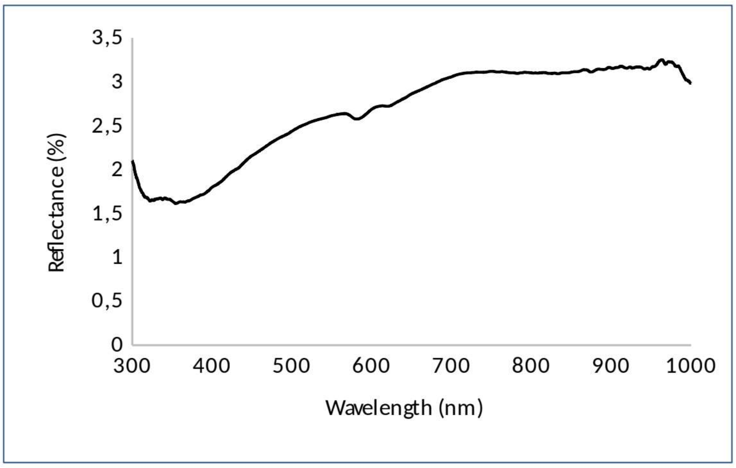


Fig. 22: reflectance spectral curve (300-1000 nm)

Observations/discussion:

The elemental analysis revealed presence of high amount of calcium (Ca), iron (Fe) and copper (Cu). The hypothesis is the presence of calcite and the Fe and Cu are probably detected from the contour, green with yellow and blue particles.

ICCROM

EXAM WORKSHEET

PROJECT THE MORA SAMPLE COLLECTION REORGANIZATION AND DESCRIPTION

GENERAL DATA
Site/object: Pompeii
Country: Italy
City: Naples
Typology: mural painting
Chronological period: Roman
Painting location: unknown

SPECIFIC DATA
Sample ID: B4F4
Description: decorative paint layer with overlapping paint layers
EXAMS
Exams: OM-Vis; colorimetry and spectrophotometry; FORS; EDXRF
Aim:
a) Register paint surface texture and details
b) First pigment characterisation
Date of the exams: March-April 2018
Responsible: Milene Gil
Executant: Cecilia Laurita

Equipment and experimental conditions:

Details of pigments particles (stable and altered within the paint layers were observed and recorded with two types of hand-held optical digital microscopes *Dinolite Premier* AD3713TB and *Dinolite* PRO AM413T-FVW working in visible inputs at 20x and 430x magnifications.

Colorimetric data were collected in all matte surface with a DataColor CheckPlusII (Lawrenceville, NJ), equipped with an integrating sphere in the following conditions: diffuse illumination 8° viewing (in agreement with the CIE publication No.15.2.Colorimetry), SCE and standard Illuminant/Observer D65/10°. The aperture size was UXAV (Ø 2.5 mm) due to small color details. The results obtained in the CIE *L*a*b** chromatic space, defined by the International Commission on Illumination (CIE) in 1976, are the average of three measurements. The chromatic coordinates measured were *L** (lightness 0-100), *a** (red/green axes 0-100) and *b** (yellow/blue hue axes 0-100).

Fiber Optics Reflectance Spectroscopy (FORS) was performed with a LR1-compact spectrometer (*aseq. intruments*, Canada) with a Toshiba TCD 1304DG linear array detector in the range of 300-1000 nm with a spectral resolution <1 nm (with 50 µm slit). Other specifications: A/D resolution 14bit; signal to noise ratio 300:1, exposure time 2.5ms-10s, CCD reading time 14m. A Fiber optMA905 to 0.22 numerical aperture single-strand optical fiber was used for the measurements and the results were treated in Lab View software.

Elemental analysis were carried out through Energy Dispersive X-Ray Fluorescence (EDXRF), using a portable Bruker Tracer III-SD spectrometer, equipped with a Rh excitation source and an X-Flash® SDD detector. The measurements were made without any filters and obtained with 40 kV high voltage, a current of 30µA and an acquisition time of 60s.

RESULTS

Fig. 23: sample overview (front) with indication of OM-Vis analysis of spot 6

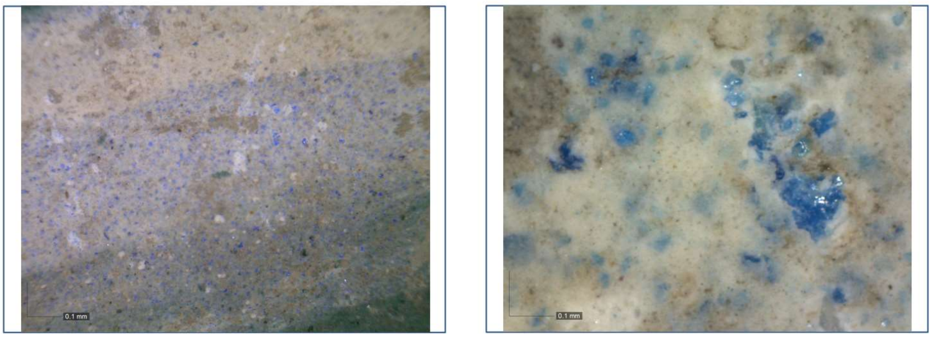


Fig. 24 a/b: spot 5 - OM in Vis (60x and 435x)

Fig. 25: sample overview (front) with indication of EDXRF analysis

Element	Line	XRF_B4_F4-1	XRF_B4_F4-2	XRF_B4_F4-3	XRF_B4_F4-4	XRF_B4_F4-5	XRF_B4_F4-6
Ca	K12	33,333	53,637	54,803	57,159	49,301	31,417
Ti	K12	0,292	0,188	0,313	0,301	0,241	0,289
V	K12	0,019	0,005	0,000	0,000	0,015	0,020
Cr	K12	2,347	0,408	0,041	0,041	0,479	1,929
Mn	K12	0,217	0,181	0,425	0,400	0,185	0,200
Fe	K12	56,489	17,638	90,348	85,725	19,669	48,345
Ni	K12	3,034	2,525	1,479	1,517	2,346	2,817
Cu	K12	2,250	0,459	0,153	0,149	13,340	1,372
Zn	K12	0,240	0,079	0,088	0,097	0,122	0,180
As	K12	0,000	0,000	1,351	1,518	0,052	0,000
Rb	K12	0,177	0,133	0,113	0,125	0,087	0,118
Sr	K12	0,617	2,246	0,551	1,034	2,174	0,665
Rh	K12	1,000	1,000	1,000	1,000	1,000	1,000
Rh	L1	1,281	1,669	1,929	1,738	1,546	1,593
Hg	L1	0,254	9,587	0,680	0,688	0,133	0,204
Hg	M1	0,029	0,123	0,076	0,054	0,036	0,028
Pb	L1	0,245	0,348	1,323	0,756	0,137	0,229
Pb	M1	0,123	0,067	0,076	0,063	0,060	0,111

Table1: EDXRF analysis results.