

A multi-analytical survey for the identification of the red and yellow pigments of coloured sherds discovered in the Monte d'Oro area (Rome).

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Abstract – The aim of the study was the characterisation of the pigments utilised on the painted sherds found during an excavation performed by the Soprintendenza Archeologica and just approximately assigned to a historical period between the first century B.C. and the first century A.D.

The analytical survey here presented meant to provide archaeologists with useful information on the painting materials to better contextualise the findings from an artistic and historical point of view. The investigation procedure comprehended the use of SEM-EDX technique and Raman, infrared and visible reflectance spectroscopies, paying most attention to portable instrumentation diagnostic performances. The study carried out on a selection of the red, and yellow sherds highlighted the presence of cinnabar, litharge, red and yellow ochre also blended among themselves or possibly utilised overlapping more painting layers. Furthermore, it is to notice the presence of gold decorations on some fragments that denotes certain care for details and opulence in the adornment.

I. INTRODUCTION

For many years now, the field of archaeological and historical studies has been interested in the contribution of scientists.

The knowledge about materials utilised in artworks creation is in fact a great way to better understand the operas themselves and the context whose they belong. In particular, in the area of the wall paintings study, that is the topic of this work, the identification of pigments and binders can be indeed a useful tool to achieve relevant information about the availability of pigments (or of raw materials to prepare them) and about the operating techniques of the old artists as well as their technological expertise. In some cases, the obtained results can also help to date the artworks and to reveal the existence of conservation works on them [1-3].

The present research is mainly focused on the identification of the colour palette of the Roman painted

walls relics found during a rescue excavation in the Monte d'Oro area in Rome and intends to integrate the context of the copious number of important studies about Roman painting materials already present in the literature.

The roughly dating of the findings, made at first sight by archaeologists, was between the first century B.C. and the first century A.D., but, since those pieces were not ascribable to any nearby ancient construction, it was not possible to assign them to a definitive artistic-historical context; the analytical survey had indeed the purpose of providing historians with useful information to attempt to fill that archaeological gap.

This work, which represents only the introductory step of a complete investigation on that archaeological area has concerned a selected collection of red and yellow fragments.

The characterisation of painting materials is commonly performed by means on the synergic utilisation of different analytical techniques and most often the achievement of comprehensive identification of the painting techniques and palettes involves both the elemental analyses and the spectroscopic techniques.

In this work, Scanning Electron Microscopy equipped with an Energy Dispersive X-ray emission detector, vibrational spectroscopies - such as Raman and Fourier Transform Infrared Spectroscopy (FTIR) - and visible reflectance measurements have been exploited. These techniques are commonly used in the field of application to cultural heritage to characterise painting materials present in different kinds of works of art [3, 4-12].

Furthermore, it is worth to underline that Raman measures were performed by means of a benchtop micro-Raman spectrometer and through a portable device too; in both cases, the analyses were made in a totally non-destructive way, namely without any sampling.

However, it is also to stress that the successful employment of the portable instrument will allow us to carry out the application of Raman spectroscopy, together with the colorimetric and spectrophotometric analyses, to a possible in-situ chemical investigation.

II. MATERIALS AND METHODS

The fragments here discussed that belong to a bigger collection of recovered decorated ancient wall painting sherds, were selected with the aid of the archaeologists involved in the Roman excavation site.

The analysed samples consist in of 7 painted wall fragments that undergone to a naked-eye exam seemed to cover the whole range of the present reddish/yellowish hues, namely bright red (two samples), red, pinkish red, orange, yellow and red/violet; moreover, they were small enough to be analysed by our Raman and SEM-EDX benchtop instrumentation without any sampling.

The SEM-EDX examinations were performed by a Hitachi TM-1000 scanning electron microscope equipped with an energy dispersive X-ray spectrometer (Oxford Instruments SwiftED) on the fragments as such: as the analyses were carried out at low vacuum condition, no coating application was required [13].

Raman analyses were carried out both by a Thermo Fisher micro-Raman iXR spectrophotometer provided with a solid-state laser emitting at 785 as excitation source and a BWTeK i-Raman EX portable device; the latter was equipped with a fibre optic probe and the source was a Nd-YAG laser emitting at 1064 nm. The entire Raman measurements were performed without any sampling, precisely directly on the sherds; all the spectra were obtained as an average of 20 scans and taken in the spectral range 200-2000 cm^{-1} .

FTIR analyses were performed by a Nicolet 380 spectrophotometer coupled with an ATR accessory Smart Orbit provided with a diamond crystal. The spectra have been acquired on micro-samples of about 1 mm^2 investigating the spectral range 500-4000 cm^{-1} with a resolution of 4 cm^{-1} . Each recorded spectrum was the result of 64 accumulations.

The identification of pigments was performed making a comparison between each FTIR or Raman spectrum from samples and the ones available in the literature.

Visible reflectance analyses were carried out, directly on different areas of the sample surfaces through a Konica Minolta CM 2300d portable spectrophotometer. The instrument was calibrated by means of its white reference (100% reflective) and zero calibration box (0% reflective).

Reflectance spectra were recorded between 400 and 700 nm.

III. RESULTS AND DISCUSSION

The SEM-EDX elemental analyses revealed on all the samples a high content of calcium, silicon, aluminium and potassium, whose signals were probably mostly coming out from the preparation layer. Besides that, each sample presented a characterising composition pattern, that allowed some preliminary hypothesis as regards the pigments present on their surfaces.

To give some examples, figure 1 displays the X-ray fluorescence spectra realised by means of SEM-EDX

technique on the orange and on the bright red II sherds.

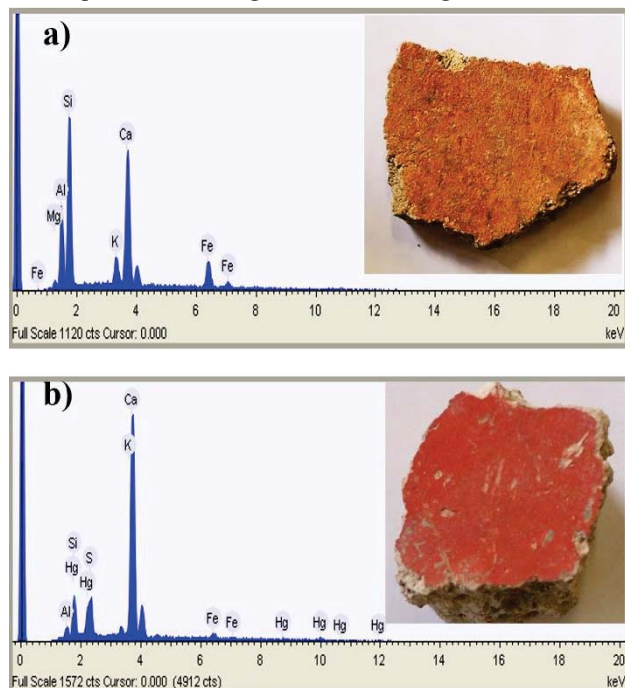


Fig. 1. SEM-EDX fluorescence spectrum of: a) orange sample and b) bright red sample II

The orange sample is characterised, besides the aforementioned main elements, by quite high iron content, that suggested the presence of a sort of ochre on that sample. On the other hand, the bright red sample II showed the presence of mercury and sulphur, that leads to think of cinnabar.

For each sample, the measurements were performed on an about 2 mm^2 area of the surface and were repeated three times moving the probe on a different position for each repetition. Table 1 shows the results of the semiquantitative chemical analyses obtained on the orange fragment; for each element, the average value and the standard deviation were also reported.

Table 1. SEM-EDX elemental analysis of orange sample

Element (wt%)	Ca	Si	Fe	Al	K	Mg
Rep 1	29,8	29,1	23,8	10,8	6,5	-
Rep 2	34,7	26,6	20,1	11,3	5,7	1,6
Rep 3	30,3	27,9	22,2	11,4	7	1,3
Avg value	31,6	27,8	22,0	11,2	6,4	1
Std Dev	2,7	1,3	1,9	0,3	0,7	0,9

Table 2 shows the compositional average values obtained on all investigated sherds.

Table 2. Main SEM-EDX elemental analysis results

Sample	Main characterising elements (w%)								
	Al	Ca	Fe	Hg	K	Mg	Pb	S	Si
bright red I	2,2	83,1	2,2	5,1	1,4	-	-	1	4,5
bright red II	2,2	54,7	3,93	27,57	1	-	-	6,03	4,6
red	2,1	72,1	13,7	-	0,7	-	4,7	-	6,8
pink	1,5	41,1	1,2	-	0,3	0,2	43	-	5,4
purple	1,8	61,6	28,6	-	0,8	0,1	-	-	6,7
orange	11,2	31,6	22,0	-	6,4	1	-	-	27,8
yellow	2,5	78,7	7,3	-	1,0	-	-	-	7,2

The bright red samples were both mainly characterised by the presence of mercury and sulphur; in addition, one of them (bright red I) also gave the unmistakable signals of gold; the latter result, that precisely consisted in a revealed percentage of gold equal to 95,4%, was not included in table 2 since it refers to a punctual analysis performed on the gilded area of the bright red sample I itself.

The pink sample gave a remarkable content in lead, whereas in all the other cases, the main component was iron, present either alone or together with some lead in variable proportion.

The presence of cinnabar on both bright red samples was then confirmed by means of Raman spectroscopy.

In figure 2a it is shown its characteristic spectrum obtained on the gilded-bright red sample.

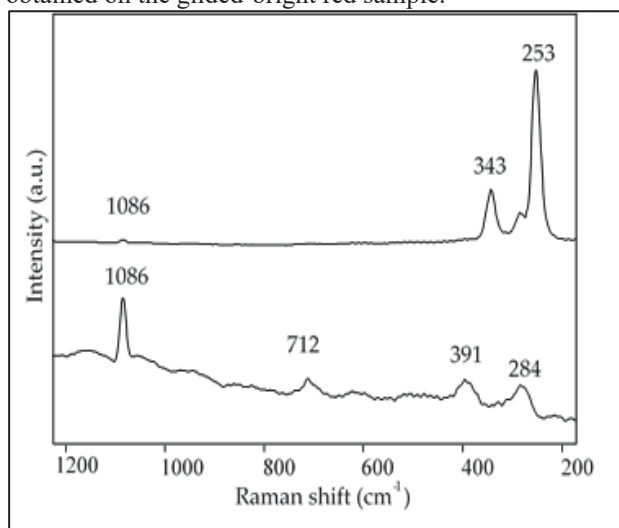


Fig. 2. Raman spectra ($\lambda_{exc}=1064$ nm) of a) bright red sample II and b) yellow sample.

Figure 2b refers to the yellow sample and indicates that yellow earth has been used; in fact, the band at 391 cm^{-1} is certainly ascribable to yellow ochre [14], whereas the

bands at 1086 , 712 and 284 cm^{-1} can surely be attributable to calcite [15]. It is worth to note that the Raman spectrum of lead oxide, precisely litharge, characterised by the very strong peak at 147 cm^{-1} [16], was obtained on the pink sample, giving a reason of a large amount of lead found on its surface (table 2).

Litharge was also revealed by means of micro-Raman analysis on a deep orange grain of the red sample, whereas the spectrum obtained on the orange sample (figure 3) appears as the overlapping of the bands of calcite (282 , 711 , 1086 cm^{-1}) [15], quartz (463 cm^{-1}), yellow ochre (shoulder at 391 cm^{-1}) [14], red ochre (291 , 405 , 605 cm^{-1}) [17] and yellow lead oxide known as massicot (143 cm^{-1}) [18].

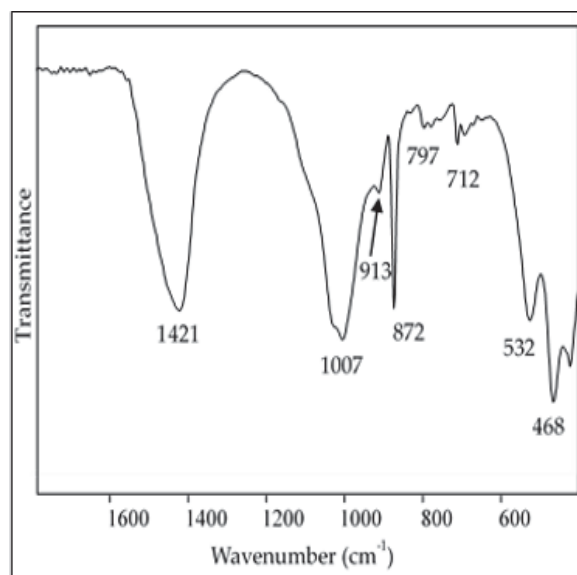


Fig.3 ATR-FTIR spectrum of orange sample

Those outcomes represent another effective example of the well-known peculiar good performance of micro-Raman spectroscopy in the identification of pigments, especially when they are obtained as mixtures of different substances [19].

The fragments were then analysed by ATR-FTIR spectroscopy. Red, pink, orange and purple red samples gave the characteristic spectra of red ochre/haematite, besides that of calcite and silicates.

Actually, the FTIR spectrum of the orange sample (figure 4) suggests the contemporary presence of a sort of yellow earth pigment because of the bands at 913 and 797 , 532 , 468 cm^{-1} , as also confirmed by the presence of the typical band of yellow ochre at 391 cm^{-1} in its Raman spectrum [14]. The presence of peaks at 1420 cm^{-1} and 871 cm^{-1} related to calcite is also observable [20].

The FTIR results achieved on the yellow sample confirmed the presence of yellow ochre as well.

It is also to stress that no Raman or FTIR signal revealed the presence of any organic material.

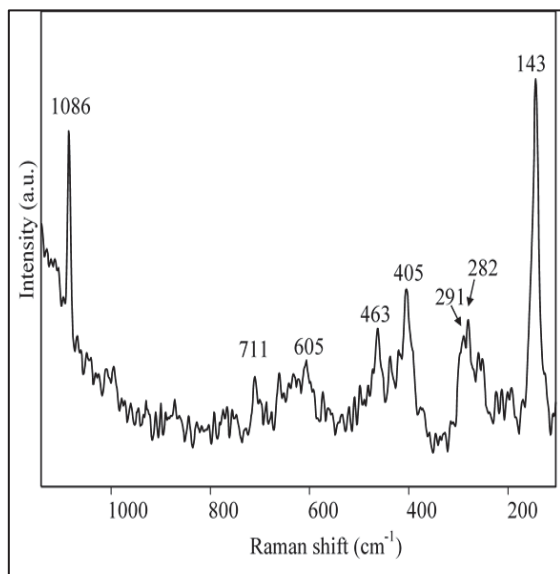


Fig. 4. Micro-Raman spectrum ($\lambda_{exc}=785\text{ nm}$) obtained on the orange sample.

Eventually, since our best goal would be the application of instrumental techniques directly on the field, besides the portable Raman spectrophotometer, a very versatile colorimeter has been employed as a visible reflectance spectrophotometer, giving some very interesting results in the discrimination of pigments, as it can be seen in figure 5, where the wide dissimilarity between the spectral features resulting from two different red samples is immediately appreciable.

The reflectance spectrum of the bright red sample I is in fact characterised by the sigmoid shape, typical of semiconductor substances such as cinnabar, whereas the purple red sample presents two main slopes at about 590 and 700 nm, that is specific for haematite [21-22].

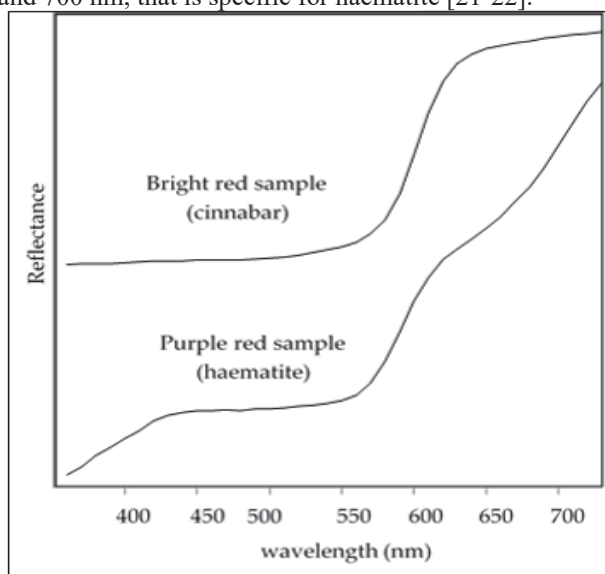


Fig. 5. Visible reflectance spectra obtained on bright red I and purple red samples

IV. CONCLUSIONS

The first notable outcome of the investigation was the total absence of organic substances in all the samples, that leads to hypothesise that the fresco technique was used for the realisation of the paintings [23].

Moreover, the chemical survey highlighted the employment of a quite multifaceted colour palette, since different pigments such as cinnabar, litharge, massicot, red and yellow ochre, in some case mixed among themselves or more probably overpainted, was used; it can therefore be stated that the attention employed in mixing or stratify different minerals in order to reach all those reddish/yellowish hues, denotes certain care for the detail of the artist.

Furthermore, it is to notice the evidence of gold details on one of the fragments, indicates a particular degree of refinement and opulence in the adornment.

Red and yellow hue shards represent the 80% of the whole amount of collected wall painting fragments of Monte d'Oro case study, demonstrating the preference in antiquity to decorate rooms with bright colours, because of the feeble illumination. Furthermore, red colour can be extraordinarily variable, as already described in literary terms by ancient authors. Despite the most accurate archaeological investigation, the results of this study show that different hues can be obtained through the use of disparate minerals, which can be verified only by means of specific analytics.

From a more technical point of view, it can be stated that a sort of strategical analytical procedure has been set up that allowed in most cases to perform the analyses rapidly and in a totally non-destructive way.

Moreover, the study surely demonstrated the possibility to carry out multiple and effective visible reflectance and Raman analyses directly on samples of a certain dimension. Therefore, the latter techniques could certainly allow such instrumental measurements on bigger samples, such as some of the other beautiful pieces collected from the excavation, that might be investigated in the future in a totally non-destructive manner.

REFERENCES

- [1] L.Bonizzoni, S.Bruni, M.Gargano, V.Guglielmi, C.Zaffino, A.Pezzotta, A.Pilato, T.Auricchio, L.Delvaux, N.Ludwig, "Use of integrated non-invasive analyses for pigment characterisation and indirect dating of old restorations on one Egyptian coffin of the XXI dynasty". *Microchem. J.*, 138, 2018, pp.122-131.
- [2] L.Bonizzoni, S.Bruni, V.Guglielmi, M. Milazzo, O. Neri, "Field and laboratory multi-technique analysis of pigments and organic painting media from an Egyptian coffin (26th dynasty)", *Archaeometry*, vol 53, No.6, 2011, pp.1212-1230
- [3] P. Fermo, A.Piazzalunga, M. De Vos, M.Andreoli, "A

- multi-analytical approach for the study of the pigments used in the wall paintings from a building complex on the Caelian Hill (Rome)" *Appl Phys A Mater.*, vol.113, No.4, 2013, pp.1109-1119.
- [4] S.A.Ruffolo, M.F.La Russa, D.Barca, A.Casoli, V.Comite, G.Nava, G.M.Crisci, A.M.De Francesco, D.Miriello, "Mineralogical, petrographic and chemical analyses for the study of the canvas "Cristo alla Colonna" from Cosenza, Italy: a case study". *Period. Mineral.* Vol.79 (Special Issue), 2010, pp.71–79.
- [5] M.F.La Russa, C.M.Belfiore, V.Comite, D.Barca, A.Bonazza, S.A.Ruffolo, G.M.Crisci, A.Pezzino, "A scientific approach to the characterisation of the painting technique of an author: the case of Raffaele Rinaldi", *Appl. Phys. A*, vol.114, 2014, pp.733–740.
- [6] C.Zaffino, V.Guglielmi, S.Faraone, A.Vinaccia, S.Bruni, "Exploiting external reflection FTIR spectroscopy for the in-situ identification of pigments and binders in illuminated manuscripts. Brochantite and posnjakite as a case study"*Spectrochim. Acta A Mol. Biomol. Spectrosc.*, vol.136, Part B, 2015, pp.1076-1085.
- [7] V.Comite, M.Ricca, "Diagnostic investigation for the study of the fresco "Madonna con il bambino", from Cosenza, southern Italy: a case study", *Rend. Online Soc. Geol. It.*, vol.38, 2016, pp.21–24.
- [8] S.Bruni, V.Guglielmi, E.Della Foglia, M.Castoldi, G.G.Bagnasco, "A non-destructive spectroscopic study of the decoration of archaeological pottery: from matt-painted bichrome ceramic sherds (southern Italy, VIII-VII B.C.) to an intact Etruscan cinerary urn", *SSpectrochim. Acta A Mol. Biomol. Spectrosc.*, 191, 2018, pp.88-97. <https://doi.org/10.1016/j.saa.2017.10.010>.
- [9] M.F.La Russa, M.Ricca, A.Cerioni, M.G.Chilosi, V.Comite, M.De Santis, N.Rovella, S.A.Ruffolo, "The colours of the Fontana di Trevi: an analytical approach", *Int. J. Archit. Herit.*, vol12 (1), 2018, 114–124.
- [10] M.F.Alberghina, A.Macchia,P.Capizzi, S.Schiavone, S.A.Ruffolo, V.Comite, M.Barberio, M.F.La Russa,"Surface and volume non-invasive methods for the structural monitoring of the bass-relief 'Madonna con Bambino' (Gorizia, Northern Italy)"*Nat. Prod. Res.*vol.33 (Issue 7), 2019, pp.1034-1039.
- [11] P.Fermo, A.Mearini, R.Bonomi, E.Arrighetti, V.Comite "Integrated analytical approach for the characterisation of repainted wooden statues dated to the fifteenth century", *Microchem J* vol.157, 2020, 105072 .
- [12] M.Gargano, L.Bonizzoni, E.Grifoni, J.Melada, V.Guglielmi, S.Bruni, N.Ludwig, "Multi-analytical investigation of panel, pigments and varnish of The Martyrdom of St. Catherine by Gaudenzio Ferrari (16th century)"*J. Cult. Herit.*, 2020.
- [13] G.Cappelletti, S.Ardizzone, P.Fermo, S.Gilardoni, "The influence of iron content on the promotion of the zircon structure and the optical properties of pink coral pigments" *J. Eur. Ceram.*, vol.25 (6), 2005, pp. 911-917.
- [14] D.Bikiaris, S.Daniilia, S.Sotiropoulou, O.Katsimbiri, E.Pavlidou, A.P.Moutsatsou, Y. Chryssoulakis, "Ochre-differentiation through micro-Raman and micro-FTIR spectroscopies: application on wall paintings at Meteora and Mount Athos, Greece", *Spectrochim Acta A: Molecular and Biomolecular Spectroscopy*, vol.56, No.1, 2000, pp.3-18.
- [15] L.Burgio, R.J.H.Clark, "Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation", *Spectrochim. Acta A*, vol.57, 2001, pp.1491–1521.
- [16] L.Burgio, R.J.H.Clark, S.Firth, "Raman spectroscopy as a means for the identification of plattnerite (PbO₂), of lead pigments and of their degradation products", *R. Soc. Chem.*, vol.126, 2001, pp.222–227.
- [17] F.Froment, A.Tournié, P.Colomban, "Raman identification of natural red to yellow pigments: ochre and iron-containing ores", *J Raman Spectrosc.* vol.39(5), 2008,pp.560 – 568.
- [18] M.Carmen Edreira, M.José Feliu, C.Fernandez - L.Martin, "J. Spectroscopic study of Egyptian blue mixed with other pigments", *Helv. Chim. Acta* 86, vol.1, 2003, pp.29-49
- [19] L.Bonizzoni, S.Bruni, A.Galli, M.Gargano, V.Guglielmi, N.Ludwig, L.Lodi, M.Martini, "Non-invasive in situ analytical techniques working in synergy: The application on graduals held in the Certosa di Pavia", *Microchem J*, vol.126, 2016, pp.172–180.
- [20] D.Gulotta, M.Bertoldi, S.Bortolotto, P.Fermo, A.Piazzalunga, L.Toniolo, "The Angera stone: A challenging conservation issue in the polluted environment of Milan (Italy)" *Environ. Earth*, vol.69 (4), 2013, pp. 1085-1094.
- [21] M.Aceto, A.Agostino, G.Fenoglio A.Idone, M.Gulmini, M.Piccolo, P.Ricciardi, J.K.Delaneyf, "Characterisation of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry", *Anal. Methods*, vol.6(5), 2014, pp.1488-1500.
- [22] M.Elias, C.Chartier, G.Prevot, H.Garay, C.Vignaud,, "The colour of ochres explained by their composition", *Mater Sci Eng B*, vol.127, 2006, pp.70–80.
- [23] I.M.Cortea, L.Ghervase, O.Țentea, A.Constantina, Pârău, R.Rădvan "First Analytical Study on Second-Century Wall Paintings from Ulpia Traiana

Sarmizegetusa: Insights on the Materials and Painting Technique”. *Int J Archit Herit* vol.14,5,

2020, pp.751–761.