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Colouring Technology Of Ancient Gandhāra; As Revealed By FTIR And XRD Analyses Of Painted Stuccos From Ogi, Mansehra – Pakistan

Mueezuddin Hakal[1] , Afeera Riaz[2] , Sidra Riaz[3]

[1]*Assistant Professor, Taxila Institute of Asian Civilizations, Quaid-i-Azam University, Islamabad.*
mueez.hakal@qau.edu.pk
[2]*MPhil Scholar, Taxila Institute of Asian Civilizations, Quaid-i-Azam University, Islamabad.*
afeerariaz@ymail.com
[3]*Scientific Officer, Drugs Testing Laboratory, Primary and Secondary Health Care Department, Lahore.*
drsidraawan@gmail.com

Abstract
The art of Buddhist sculptures were added with the paintings of different colours in Kushana age Hellenistic culture, between the first to fourth/fifth centuries CE. These stylistic expressions in stone and stucco were common among the Gandhāran artists, as similar intact evidences in stucco from Mes Aynak have marked in Afghanistan. In this connection, we were fortunate for having two stucco pieces of this period, found from a site around Ogi in Mansehra. These broken stucco shards were collected by some locals and forwarded to us with hand to hand information of their location. These broken two pieces are undoubtedly from a stucco sculpture, interestingly intact their red-orange colour over the white. Therefore, we aimed to understand the applied technology of colours' manufacturing in antiquity. Thus, in order to know this aspect of ancient technology, we mainly applied the analytical technique of Fourier Transform Infra-Red Spectroscopy (FTIR) with additional support from X-ray Diffraction (XRD) to confirm the results. Using this multi-technique investigation to characterise pigments and paint binders of the base stucco layer, painted layer and covered dust layer allowed us to identify the composition of the materials employed in the paint production, as indicated by the samples. Besides FTIR, the X-ray Diffraction technique added that the iron is the principal element (the ratio Fe/Mn is higher) in the red-pigmented surface. Therefore, this study concludes that the red ochre was used to manufacture the red-orange paint, as the main ingredient, beside other miscellaneous additions with the oil. Thus, this study reveals that the oil-based paint was utilised at Ogi to colour the stucco sculptures.

Keywords: Ogi, Gandhāra, Ancient Colouring Technology, FTIR, XRD, Red Oil Colour, Ochre.

1. Introduction

The complex data of ancient painted artefacts, with intact colours are discovered from various sites, with variation in their deterioration depending on the nature of material, location and environment, and on the length of time. Therefore, if we have an overview of the ancient data from the Gandāran sites (Cunningham 1871) in Taxila, Peshawar, Swat, and Afghanistan (Foucher 1917, Coomaraswamy 1927, Hallade and Hinz 1968, Murthy 1977, Zwalf 1996, Behrendt 2007, Klimburg-Salter 2018), the intactness of colours of sculptures vary from region to region, depending on the material, dry environment suitable to give a longer life to the painted material and the age of antiquity. Therefore, it primarily depends on the colour's nature, which elongates the life, even in a moist environment such as that in Hazara, Pakistan. Previously, a similar data from different sites in Pakistan and Afghanistan (Samad 2011, Ball 2019) have been collected and studied based on scientific methods (Pannuzi et al. 2019). Analysing the data of this nature is a complex task for answering the related academic questions. Therefore, still we are at the beginning in answering the questions relevant to colours manufacturing technology, and the concepts connected to their evolution in Gandhāra. Further, understanding the composition of intact colours is a complex task, because the colours might be composed of amorphous (Goodall et al. 2007: 670) or crystalline (Sansonetti 2016: 1057) with a variety of major and minor mixtures, which are delicately organised or arranged in a multi-layered application of different colours and their mixtures. In order to explore the hidden information in arts through technology, it has been presented with diverse solutions through micro-imaging techniques. The use of technology is a compelling analytical platform to deal with different molecular and structural compositions of painted materials. In this regard, the use of technology helps in elaborating the two-dimensional atomic and subatomic structure of pigments and binders (FitzHugh 1997, Edwards et al. 2006). Therefore, it gives a better idea of the composition at a micro-resolution to explore more about ancient technologies (Škapin et al. 2007, Pannuzi et al. 2019).

In this regard, we received two broken pieces of stucco 'a' and 'b' from Mr Iftikhar of Taxila (Fig. 2), which reached him through different hands, with only information of its collection from a site around Ogi. The town of Ogi is located in District Mansehra (Hazara Division) of Khyber Pakhtunkhwa Province, Pakistan. Previously in 2014, the Department of Archaeology, University of Hazara, visited this area for field activities. Where, in the vicinities of town Ogi, they explored four sites of the Buddhist period, namely Gharryaan, Nawab Di Haveli, Dhari Kolay and Podnul (Fig. 2), and few more but away from the town.

2. Material and Methods

The stucco sherds 'a' and 'b' appear to be the broken parts of a sculpture, with uniform grooved impressions of depicted drapery. The drapery was coloured red-orange to represent the monastic robe of the figure, as the use of this colour can be generalised from the references of robe depictions at Mess-Ayank (Figs. 3 and 4), Afghanistan (Klimburg-Salter 2018, Nagaoka 2020, Kijima 2021), a painted silk banner from Dunhuang (Whitfield 2004, Wang et al. 2021), and a few more examples from Central Asia (Muzio 2008). The use of this colour still continues in various Buddhist traditions around the globe.

In order to obtain more accurate results, based on an academic hypothesis of the possible use of red ochre for this painting, based on previous studies (Pannuzi 2019: 73). For the study of this colour we have the only option of a laboratory-based analysis. Therefore, this study is carried out keeping two objectives in view. The first objective is to understand the primary source materials of this colour, and the second is to explore other miscellaneous ingredients utilised to strengthen and improve the primary colour's quality.

The procedure of a laboratory-based study involves the utilisation of iron scale, vernier calliper, petri-plates, microscopic slides, a microscope of 40x and further FTIR tool. In laboratory, firstly, measurements of both broken red-orange coloured pieces of stucco are taken with a vernier calliper. It is measured that the stucco piece ‘a’ has an average width of 51.08 mm, length of 55.55 mm, and thickness of 28.74 mm, and stucco piece ‘b’ has an average width of 54.38 mm, length of 71.79 mm and thickness of 20.44 mm.

Further, it was necessary to remove the upper layer of the super-deposited microscopic layer for the analysis in a controlled environment for exploring layer by layer information. Under this condition, we removed the upper layers of apparent dust from both stucco pieces and samples collected for the study. While collecting the samples, we noticed that the top surface of the stuccos appeared to be brown, which shows that both pieces (Figs. 5, 6 and 7) remained under the thick deposition of soil and/or sand. Furthermore, the sample collected from grooved curves of the stucco underneath the top layer of dust (layer ‘2’) appeared to be red-orange, different from layer ‘3’, a base layer of white stucco. Hence, the isolated samples were collected separately from each layer with distinctive features, ready to be compared with the spectra library.

From every distinctive stratum ‘1’, ‘2’ and ‘3’, the samples were extracted using small-sized brushes and spatulas and gathered on fine plain paper. Further, small 1.5 ml micro-tubes were utilised to store the sample, keeping the safety measures to avoid contaminations (Figs. 8a and 8b). Additionally separate microscopic slides were prepared for each sample, to study all pigments and the existence of any contamination under the microscope (Figs. 9a and 9b) for FTIR analysis. It was noticed that the extracted sample from each stucco shard was not enough in quantity for FTIR analysis; therefore, samples collected from both stucco pieces were then mixed as one to continue the procedure. This method aims to obtain a thin layer that is easier to be observed under a microscope.

The FTIR technique (Bikiaris et al. 1999, Edwards et al. 2006) is often used to analyse the painting techniques and cross-sections of the binders and the pigments. This analytical technique can give a better result, if the sample is carefully prepared and preceded for data analysis without damaging. In the FTIR technique, a thin film of the specimen is placed under the plunger while using the modes of ‘transmission’ and ‘absorbance’. It is essential to consider that the better signal quality is significant for readings in transmission and absorption modes. In the following steps, the produced signals are then converted into interferograms, which is used to analyse all three layers. Every time, the spectra are recorded by the OPUS software. However, there are possibilities of sharing the remains of upper layers in lower, even after careful extraction, may interrupt the signals and could affect the results of FTIR and thus can hinder our analysis.

3. Analyses

The FTIR measurement is carried out using an Alpha Platinum ATR-FTIR spectrometer. The samples from all three layers, ‘1’, ‘2’ and ‘3’, are placed under the plunger in FTIR-spectrometer’s sample compartment. Then signals are sent to the system to record the results in transmission and absorbance modes. The spectra between 400 - 4000 cm^{-1} are acquired in the spectral resolution of 4 cm^{-1} and 128 accumulations, under resolution 2 cm^{-1} within 20 scans per minute. All spectra obtained reveal typical patterns, even though some differences in the intensities and widths of the absorption bands. All three pigments of stucco ‘1’, ‘2’ and ‘3’ are analysed to obtain (spectrums) interferograms.

The layer ‘1’ interferogram shows a strong-wide band in the range 1330-1600 cm^{-1} wavenumber. Several peaks in the spectra of Layer ‘1’ (dust layer) lignins are also observed between 1600

cm^{-1} and 1500 cm^{-1}, which is a maximum range of absorption band. The intensities of the absorption band at 1600 cm^{-1} and 1500 cm^{-1} are nearly equal. However, there is an intense absorption band falling in the range between 1400 - 1300 cm^{-1} with a high rise peak at 1408 cm^{-1}; most possibly, this may be caused by the absorption of the liquid paraffin. In layer 1, different copper compounds, such as copper oxalates (doublet nmax/cm-1 1363 - 1319), are observed. The large C¼O stretching band (nmax/cm-1~1568) is associated with metallic carboxylates.

Nevertheless, similarities and differences can be observed in all three cases. A similar feature in spectra '1' to '3' C¼O ester (n_{max}/cm^{-1} ~1740) stretching modes supports identifying an oily binder. In layers '1' and '2', a blend of copper and lead soap can be hypothesised, considering the shape and position of the mixture. The existence of copper oxalates in upper layer '1' could be a penetration in lower painted layer '2' due to ageing. Layers '1' and '2' also contain proteins (characteristic amide I band around nmax/cm-1 1650) and polysaccharides (C-O stretching around nmax/cm-1 1050). The existence of proteins helps us assume the use of mucilage and/or protein-based material, such as hide glue or egg.

Pigments such as Hematite are identified through the characteristics O-H stretching at n_{max}/cm^{-1} 1000 - 800, concentrated in layer '2' (paint layer). In layer '2', some high spots of Hematite are observed, corresponding to white grains discernible in the visible picture. On the other hand, Cerussite ($PbCO_3$), usually associated with hydrocerussite in lead white, is almost concentrated in the white layer '3'.

In layer 3, the red-orange colour is partially due to goethite (FeOOH), identified by the doublet n_{max}/cm^{-1} 896 - 796. The signals from layer '2' and '3', in particular C¼O acid stretching (n_{max}/cm^{-1}~1702), is typical of a natural resin (such as mastic). Characteristic vibration signals were used to draw the distribution of the different components, pigments and binders.

Furthermore, the graphs obtained from powder X-ray Diffraction further confirm the presence of Hematite or Ochre in layer '2' and several new peaks that can be seen in Fig. 10.

4. Discussion

The Gandhāran stucco art gradually started to evolve from the Scytho-Parthian period to its maturity during the period of later Kushanas between the third and fourth century CE. This tradition continues beside the emergence of the Mahayana tradition (Zwalf 1996: 32-33) of Buddhist philosophy between 127 to 151 CE, focusing on the figural expression of the Buddhist tradition. The stucco as a medium for work of art, amalgamating the Hellenistic medium to express the Buddhist philosophy (Brown 1942: 41-43), is emerging despite the decline of art execution in stone (Shahab 2015). In general, these broken pieces of art reached to us can be dated around the same period of later Kushanas. Stucco, due to its sophistic nature for art execution, can be more easily moulded (Andrew et al. 1996: 365), which gradually replaces that in the stone (Shahab 2018, Rosa et al. 2019). The prime material of this work is lime, and experiments have shown the use of other organic substances to add sophistication to artwork (Lluveras-Tenorio et al. 2022). The present evidence and many more examples have collectively helped us to understand the addition of colours over the stucco sculptures in beautifying and bringing the art very near to nature.

To add and understand more to the known science of colouring technology of Gandhāran artists, we have a deeper look into this available fresh data. Therefore, with the help of scientific tools of analysis of these applied colours over the stucco, add and endorse the known details of colour compositions, mainly concerning the compositions of red-orange colour. The results of this study reveal the presence of a broad range of compounds, with a high diversity not only in pigments but also in the pigment binders. Stucco pieces, in our study, portray the total stratigraphy with valuable information in the form of interferograms. Unfortunately, there is no direct method to portray the presence of these possible unique binders such as (goethite) and adjustment compounds. However, with the help of FTIR analysis, pigments and binders simultaneously can be distinguished.

The fluctuating extents of these parts in the form of peaks of interferograms are likewise demonstrative of complicated artistic, creative procedures and painting techniques used in Gandhāra. In previous studies, ochre was the most frequently found pigment for the composition of red-orange pigments, besides aluminium-silicates with different amounts of a crystallised water-binding strict relation between silicon, iron and magnesium (Pannuzi et al. 2019: 73-74). The use of red ochre in painted examples can be dated back to the 300,000 years before the present time and has been continuously used throughout the ages for depicting the artistic expressions (Schmandt-Besserat 1980). This study created a base to believe that minimum a red oxide was also employed to create this colour, besides confusion in the usage of litharge and massicot (Pannuzi et al. 2019: 74). Therefore, this study endorses the previous understanding of using red ochre to create this colour (Lluveras-Tenorio et al. 2022) and adds that the inclusion of protein-based material can be hide glue or egg. Besides this, the evidence of the inclusion of oil binder in the composition of all layers is also visible. This finding adds to our concept of using oil-based colour with the mixture of ochre as the significant ingredient besides the protein-based material and the usage of natural resin. However, copper oxalates in the upper layer can also be part of this colour. This ongoing undertaking reveals another insight into highly creative and aesthetic oil painting practices used fifteen centuries ago, before the invasion of White Huns on Gandhāra in the fifth century CE. The nature of oil paint can be a reason of intact colour for an extended period. However, further inquiries are still needed on the selection of particular paints, specific colours, their makings, related paint binders, and details on their utilisation and blend, through experimental archaeology (Kenoyer 1994).

The presence of lead in artefacts still raises many questions; for instance, the variously reported metallic carboxylates from the old murals result from a deliberate amalgamation of synthetically synthesised Lead compounds or a long modification with oil and minerals; this research question is not yet answered. Studies (Pannuzi et al. 2019) also suggest the dynamic proportion of hydrocerussite and cerussite, these two lead carbonates being constitutive of lead white. However, there are questions about the proportions to make lead white; different and distinctive utilisation of the same lead white, blended with oil and paint binders; synthetically changing it in different proportions. Much detailed work still needed to be carried out to respond to these inquiries to uncover every hidden secret kept in these old artefacts and their complex compositions.

5. Conclusions

The use of multi-techniques investigation for characterisation of both pigments and paint binders in the painted layer allowed us to identify the composition of the materials employed in the production of the red-orange paint coloured over stucco from the Gandhāran culture, as indicated by the evidence from the Ogi in Mansehra, Pakistan. This study of three distinct layers with brownish super-imposed layer ‘1’, red-orange coloured layer ‘2’, and white stucco base layer ‘3’ have revealed distinctive results besides sharing common features.

1. In layers ‘1’ to ‘3’, stretching modes supported the identification of an oily binder.
2. In top layer ‘1’ various copper compounds such as copper oxalates are evident beside the absorption of the liquid paraffin.
3. Layers ‘1’ and ‘2’ contain a mixture of proteins and polysaccharides besides a thick concentration of Hematite in layer ‘2’.
4. In layers ‘2’ and ‘3’, natural resin (such as mastic) is evident.
5. In layer ‘3’, the red colour is partial due to goethite (FeOOH), whereas lead white is concentrated.

Thus, this study concludes that the red ochre was used to manufacture the paint as the primary ingredient, with the inclusion of protein-based material, oil binder, natural resin, and copper oxalates. Therefore, we can believe that the Gandhāran artists used oil paints for art activities in colouring the stucco sculptures.

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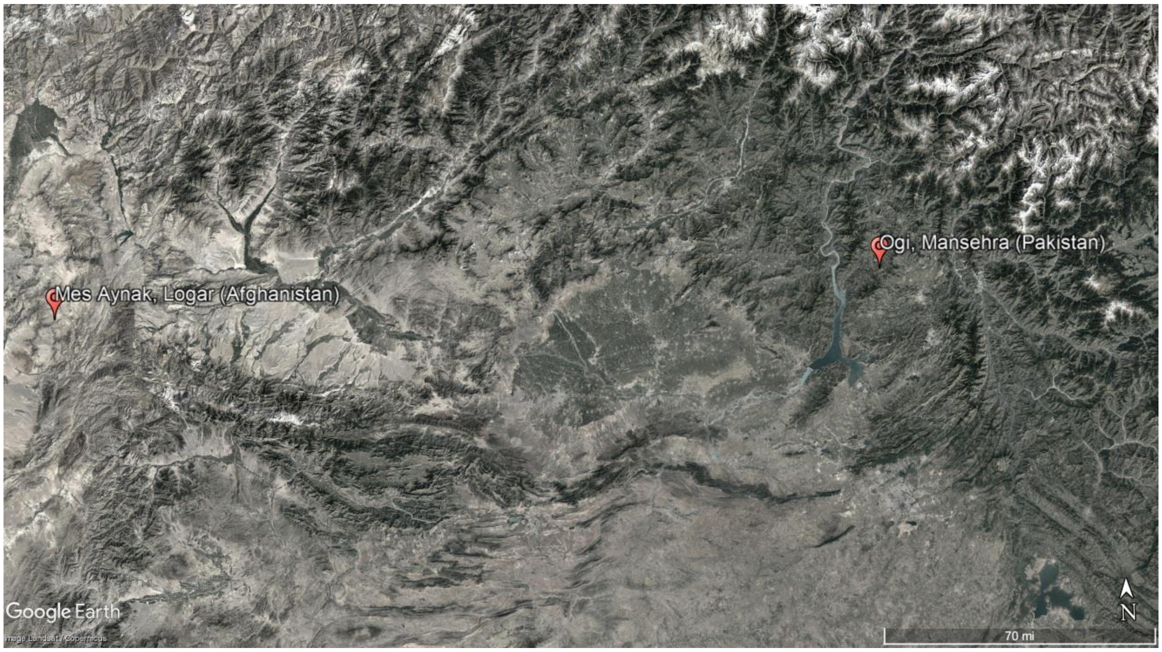

Fig. 1 - Location map of Mes Aynak (Afghanistan) and Ogi Town (Pakistan).
(Location map marked on Google Earth)

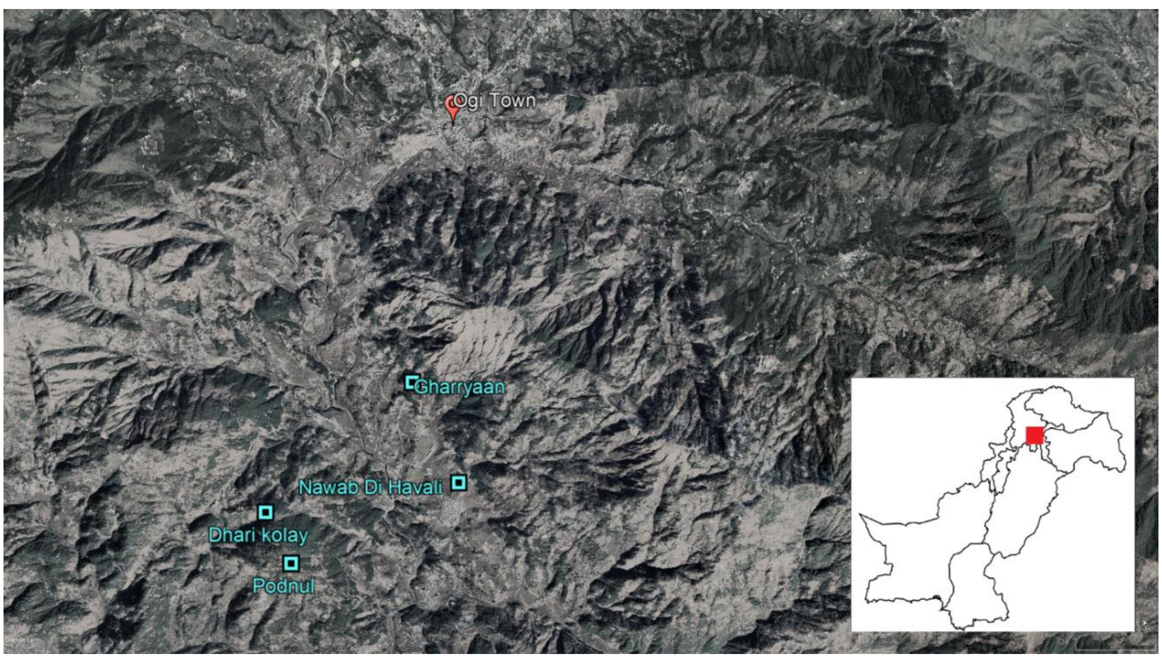

Fig. 2 - Archaeological sites in the vicinity of Ogi Town, Explored by University of Hazara, 2014.
(Location map marked on Google Earth)

Fig. 3 - A huge archaeological complex of Mes Aynak site, Afghanistan (Photo by Hakal).

Fig. 4 - Red-Orange coloured monastic robes from Mes Aynak (Photo by Hakal).

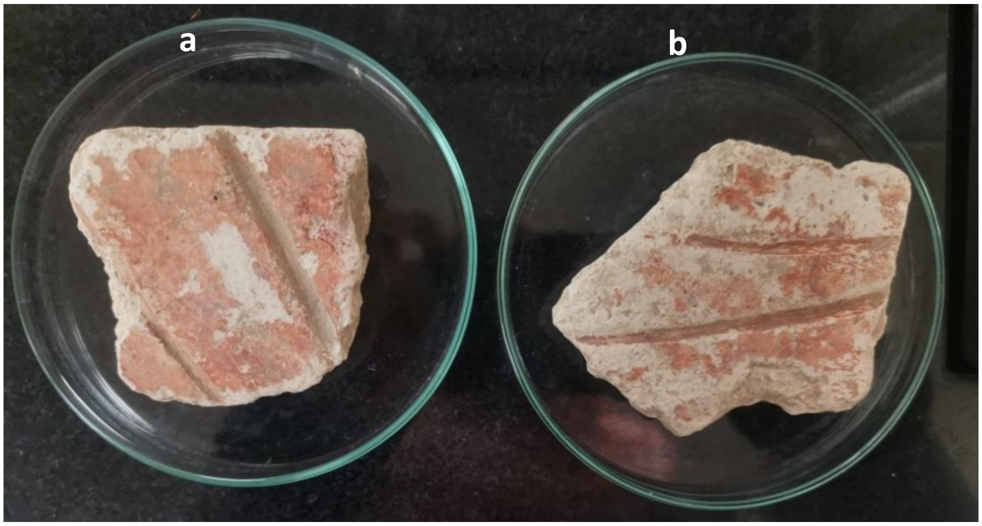

Fig. 5 - Stucco (a) and Stucco (b).

Fig. 6 – Average widths (a) and length (b) of stucco pieces with red colour.

Fig. 7 - Scratching of pigments from stucco (b): (1) brown Pigment (dust sample), (2) red Pigment and (3) white pigment (base material).

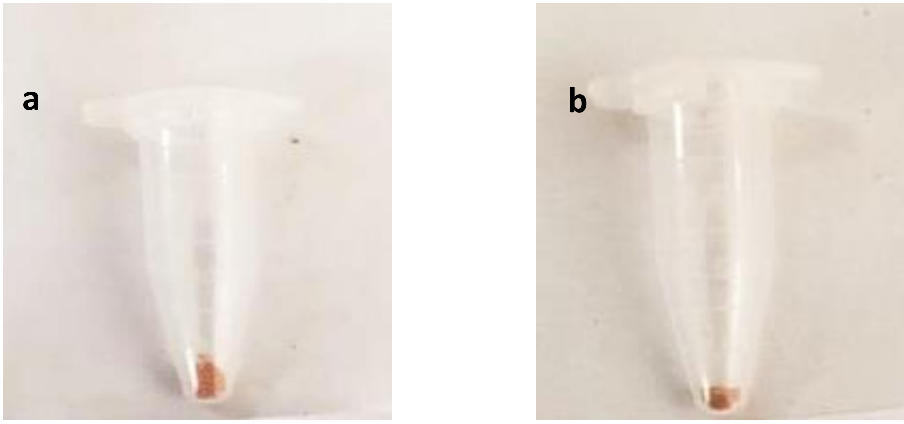

Fig. 8 a - Sample stored of stucco a.
Fig. 8 b - Sample stored of Stucco b.

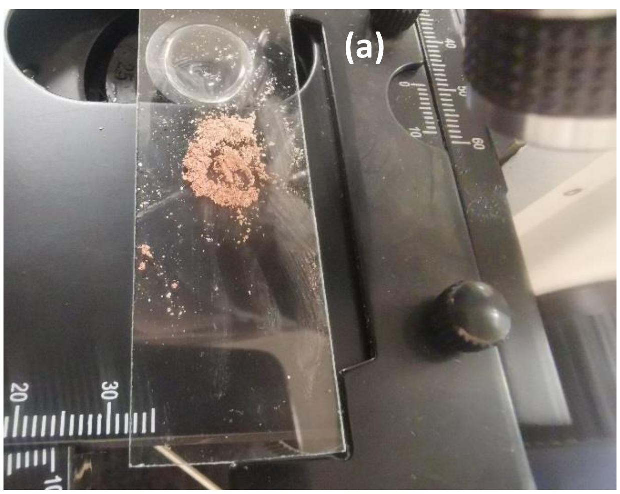

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Fig. 9 a - Red paint pigment (sample a) on slide, placed on stage of microscope.

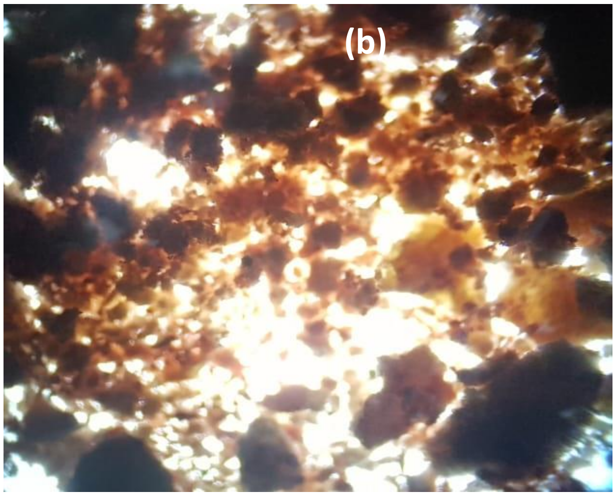


Fig. 9 b - The view of slide under a Microscope at 40x resolution.

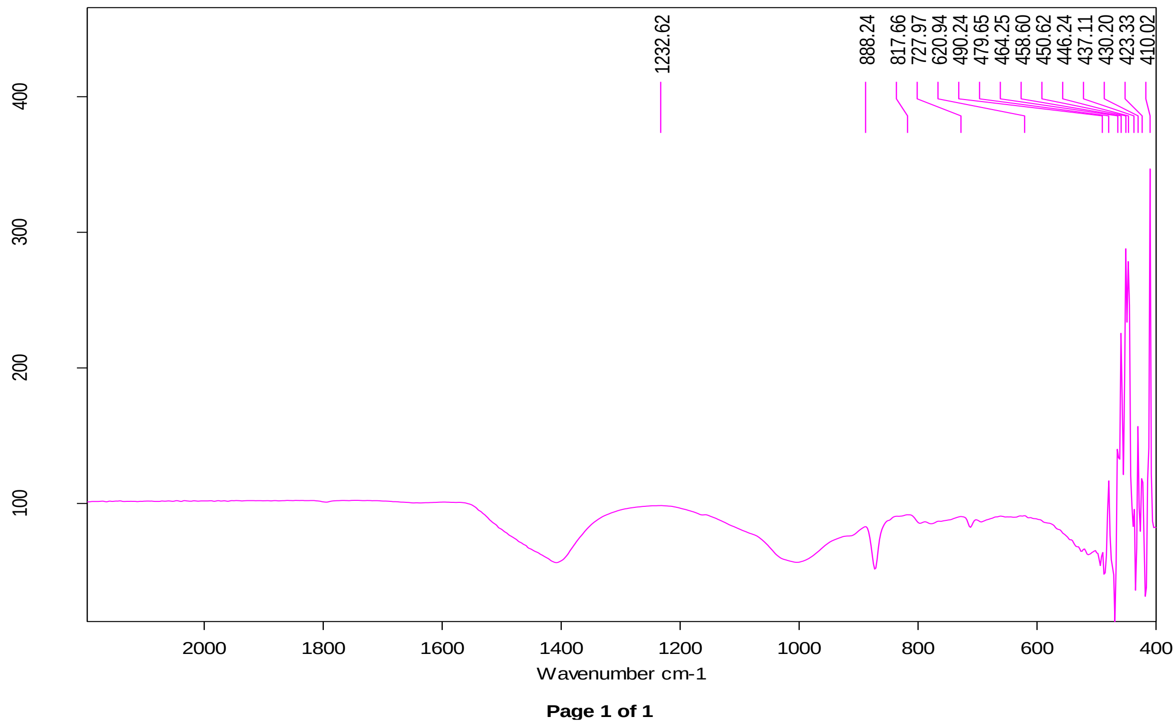


Fig. 10 a - Brown pigment (layer 1) Transmittance.

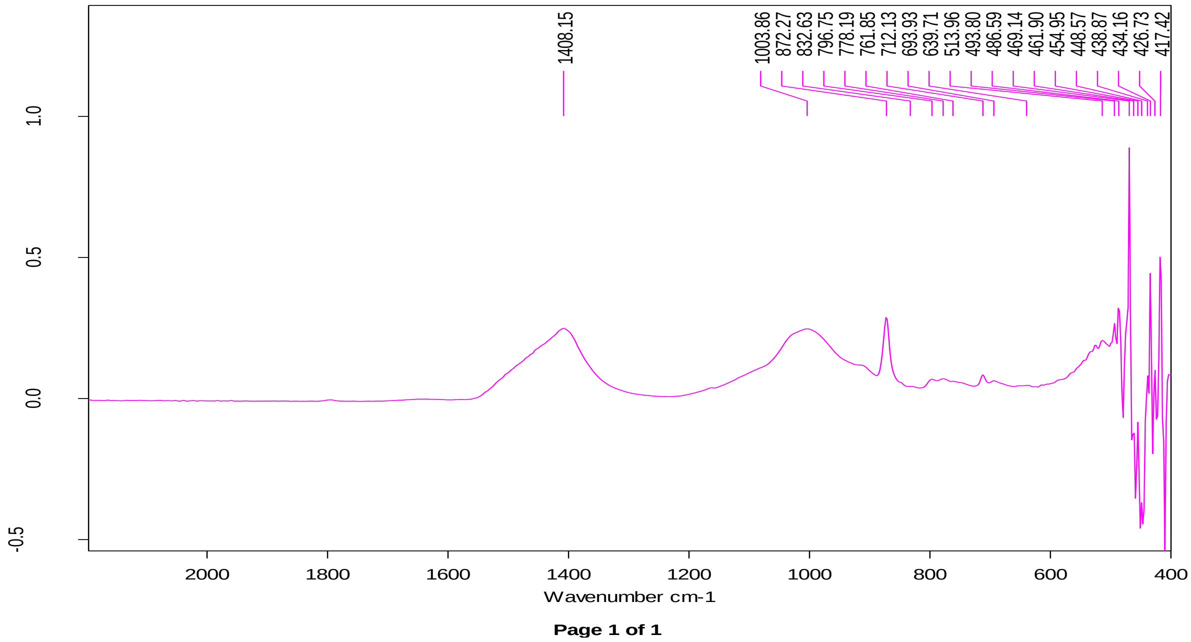


Fig. 10 b - Brown pigment (layer 1) Absorbance.

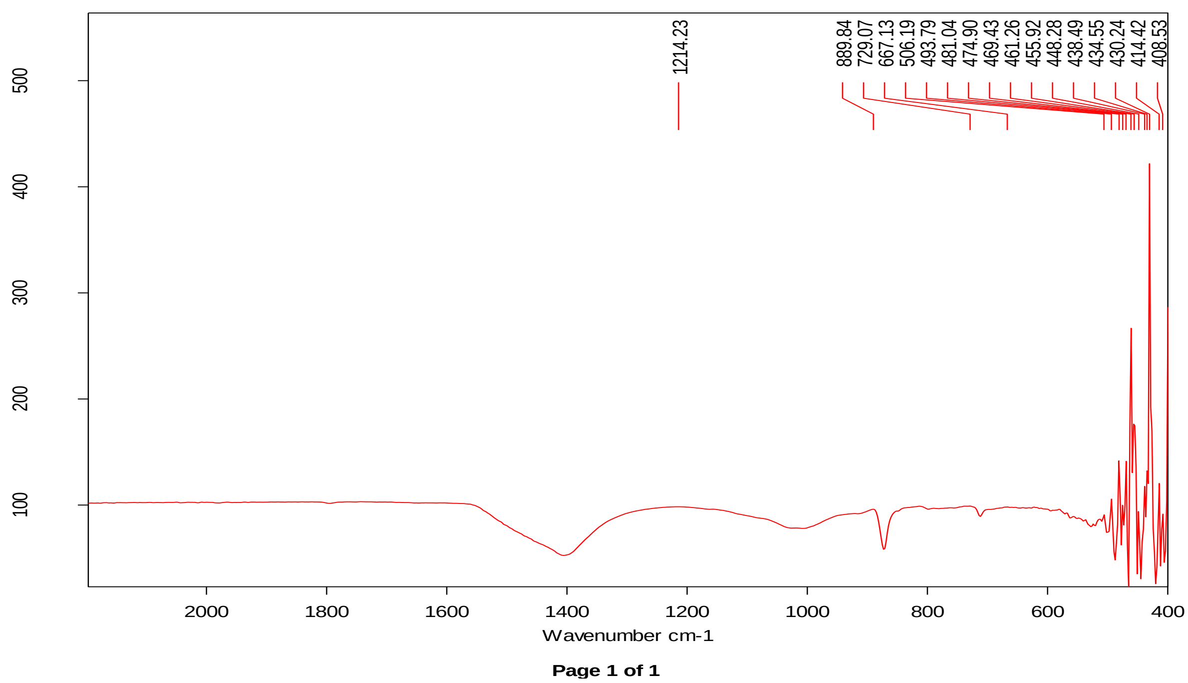


Fig. 11 a - Red Pigment (layer 2) Transmittance.

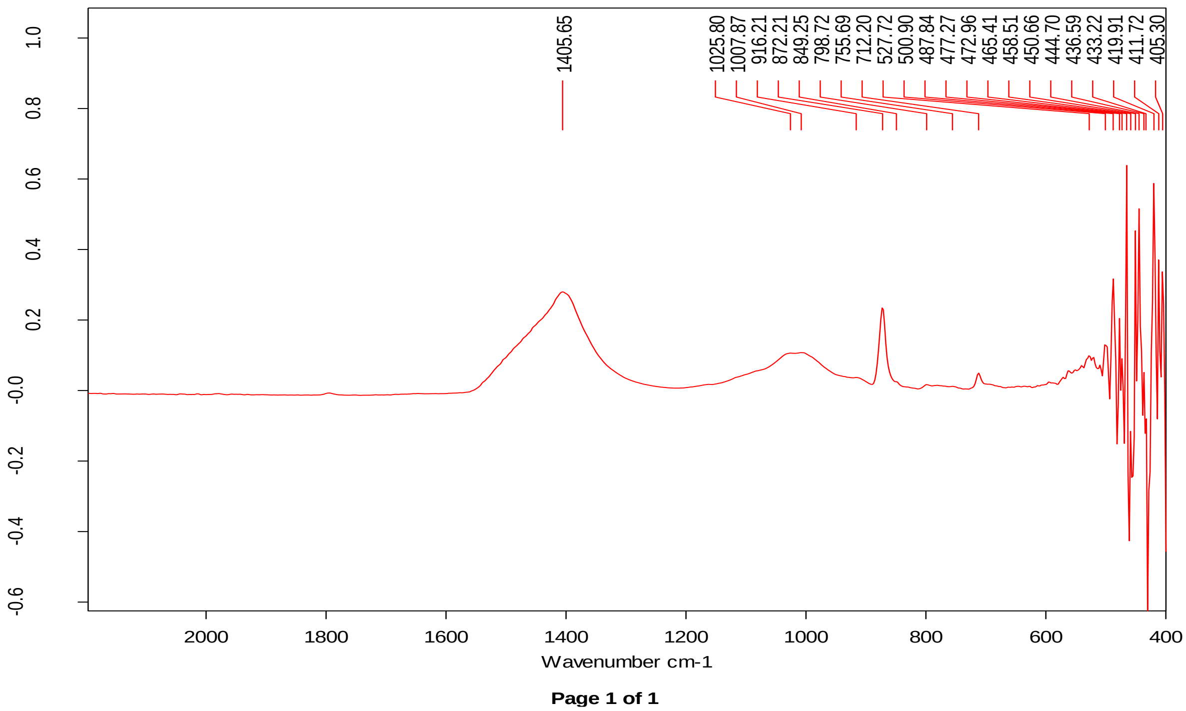


Fig. 11 b - Red Pigment (layer 2) Absorbance.

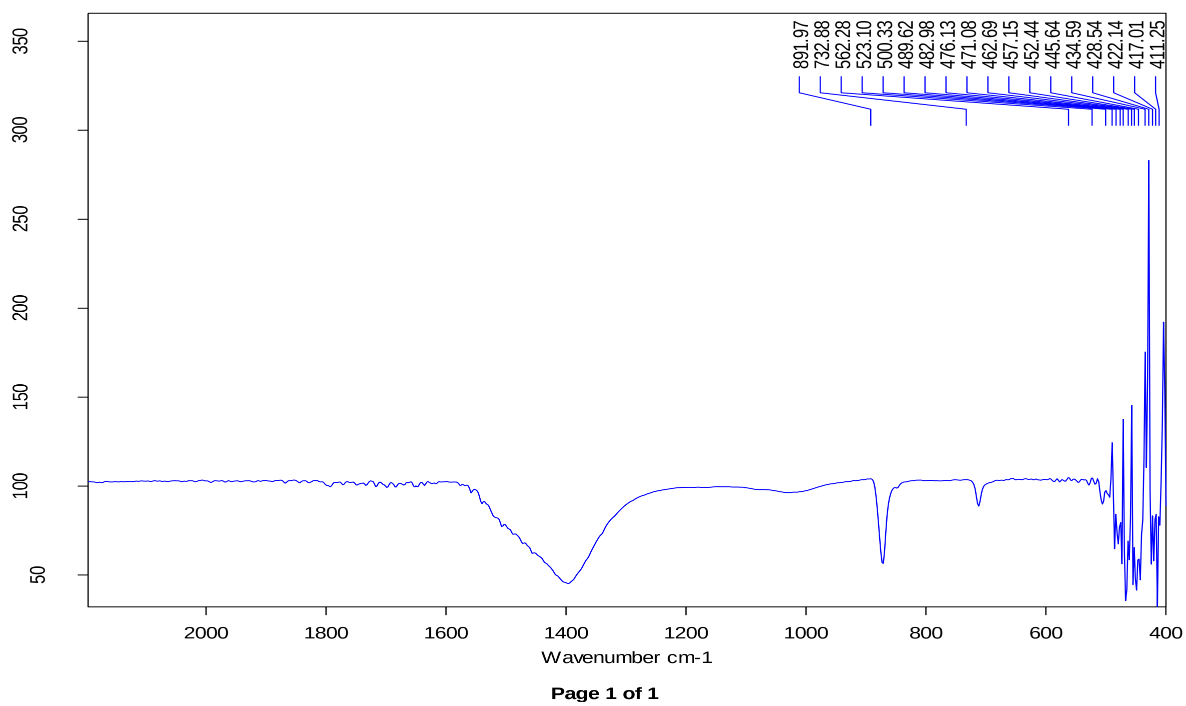


Fig. 12 a - White pigment (layer 3) Transmittance.

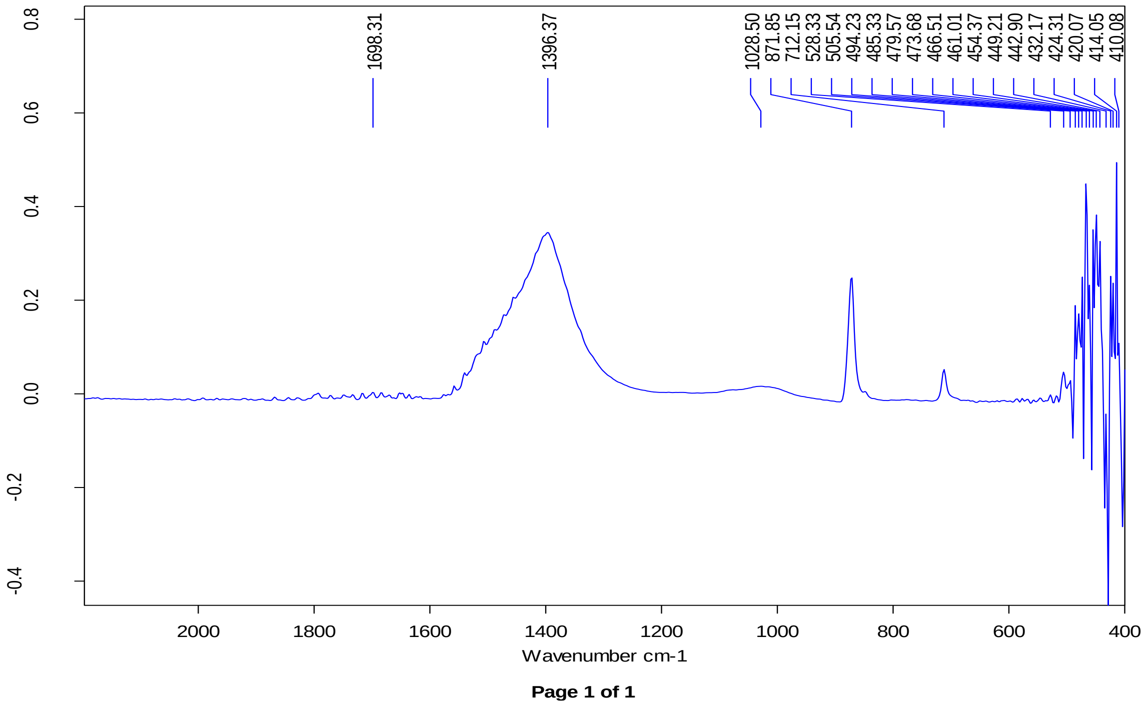
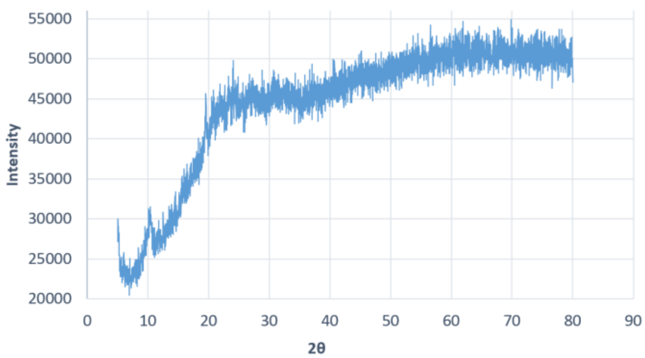
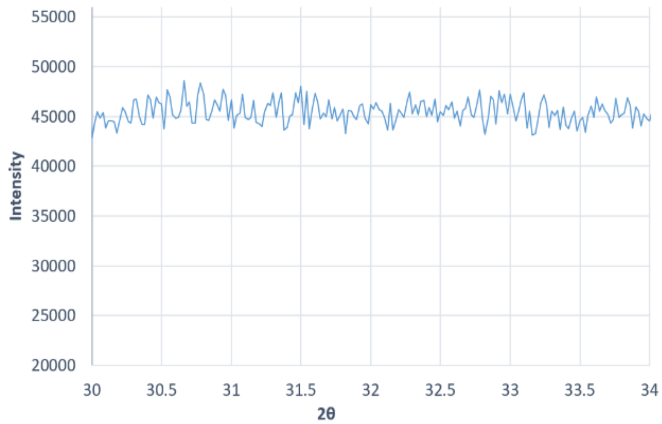


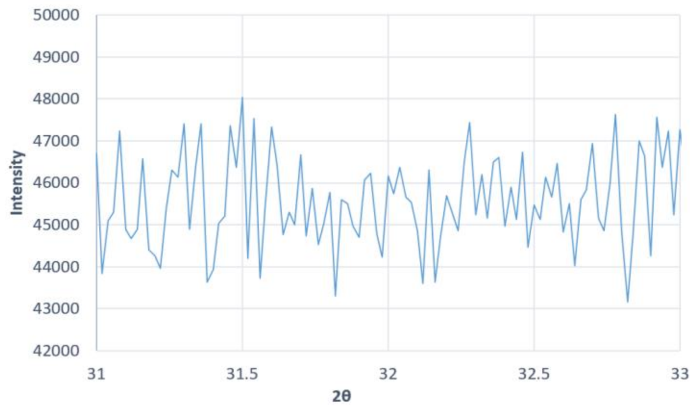
Fig. 12 b - White pigment (layer 3) Absorbance.



(1)



(2)



(3)

Fig. 13 – XRD graphs.