Spectroscopic and Non-destructive Analysis Methods for Investigation of Inorganic Pigments on Historical Wooden Objects in North of Iran

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Abstract

In this research, the characterization of very stable pigments from a cultural heritage building named by *Saghatalar* which is located in Mazandaran province, a suburb around of Fridonkenar city in the north of Iran near Caspian Sea (Cochakbishehmahaleh village) was investigated. For this investigation, the wood samples were given from *Saghatalar* for characterization and analysis. The result were showed no organic materials was find in the four colours (blue, red, yellow and green) as samples of this building were detected and taken. Fourier transform infrared spectroscopy (FT-IR), X-ray fluorescence spectroscopy (XRF), X-ray emission spectroscopy (XRD), Uv-vis spectroscopy, fluorescence spectroscopy, Raman spectroscopy and Mossbauer spectroscopy have been used for determination of kind of dyes in *Saghatalar* wood.

Keywords: Iran's Cultural Heritage, Saghatalar, Mazandaran province, X-ray, spectroscopy, Raman spectroscopy.

Introduction

There is no indication of the direct use of wood by the earliest hominids, although Neanderthals exhibited much complex behaviour such as funerary practices (Errico *et al.* 2012). Cultural uses of wood appear to be related to the activity of humans rather than hominids (Bamford 2010). Any wooden artefact that provides us information about human life and culture, and that is considered worthy of preservation for the future can be defined as wooden cultural heritage (WCH) (Rowell 1990). Vocational, technical artefacts, creative activities, and cannons of craftsmanship are embedded in WCH, reflecting past human culture, ideals, and symbols. Thus, the technological and sociological aspects of human activities can be understood from excavating WCH objects or remains. Wooden artifacts, wood painted panels and historic furniture represent a significant part of our cultural heritage. Their preservation over time is a challenging task as they can be damaged by several chemical–physical, mechanical and biological phenomena. The last ones are particularly relevant in causing damage, given the organic composition of wood. The microbiological activity of bacteria and fungi results in aesthetic alterations and depletion of mechanical characteristics, but insect infestation still represents a primary cause of loss of cultural heritage artifacts.

In the past, several chemical methods mainly based on the use of liquid preservatives or gaseous fumigants have been used for the conservation of wood under insect attack (Unger 2012). Such treatments present numerous negative drawbacks, including a high risk of damaging the objects (Wörle *et al*. 2012) and serious safety issues for operators due to chemical toxicity. Less dangerous alternatives have, therefore, been proposed and tested, including thermal treatment (using either low or high temperature) (Strang 1995), physical methods (microwaves, X-rays and gamma rays irradiation) (Andreuccetti *et al.* 1995; Augelli *et al.* 2007) and the use of controlled atmosphere (Unger *et al.* 2001). The colour in Cultural Heritage represents one of the latest international and interdisciplinary efforts in perfecting documentation of extant material cultural heritage. In the field of art conservation, the need to study colour and its variations became particularly evident in the second half of the 19th century when, following remarkable developments in the chemical industry, artists were provided with ready to use pigments/dyes (Bacci *et al.* 2006). Amongst scientific methods introduced to art conservation the measurement of the colour of any material or surface of artwork has been increasingly used from the 1930s (Barnes 1938; Johnston 1967; Bullock 1978).

A multi-technique analytical approach for the identification of pigments used to create wall paintings is crucial for a deeper knowledge of raw materials, manufacturing techniques and preservation methodology. Several works have been recently published on the characterization of pigments from cultural heritage artifacts using Fiber Optics Reflectance Spectroscopy (FORS) and Raman and X-Ray Fluorescence (XRF) portable equipment (Cheilakou *et al.* 2014; Aceto *et al.* 2014; Appolonia *et al.* 2009; Bracci *et al.* 2009 Syta *et al.* 2014: Madariaga *et al.* 2014), which are applied together in some cases. The imaging spectroscopy techniques can be effectively used for the identification of materials in artwork. The recent advances in the spectro-imaging field in addition to the demand for non-invasive techniques in the study of cultural heritage materials offer a favourable condition for the development of these methods. However, these techniques are usually not conclusive for identifying pigments; thus, confirmation of the composition through other experimental techniques is required. The inadequacies of FORS are observed when mixtures of pigments or organic binders are present (Cheilakou *et al.* 2014; Appolonia *et al.* 2009). XRF is elemental analytical technique that only yields information about key chemical elements. The employment of Raman

equipment is only reliable when absolute stability is reached, and analysis using this technique takes a long time. In addition, the sensitivity and lateral resolution does not typically allow for the obtaining of information about all layers of the polychrome painting (Perez-Rodriguez *et al.* 2014). Some pigments also fail to produce an identifiable Raman spectrum, and others do not even produce a detectable signal (Duran *et al.* 2011). To overcome these difficulties, we have employed X-Ray Diffraction (XRD) in this work using a portable system, together with FORS and XRF. Only a few XRD portable systems are available at present (Beck *et al.* 2014; Mendoza-Cuevas *et al.* 2015; Nakai and Abe 2012; Pappalardo *et al.* 2008). XRD is the most consistent technique for the identification of crystalline materials, allowing for the identification of each component in a mixture.

The aim of the present work is to analysis several fragments of Roman wall paintings from an archaeological excavation of the Reales Alcazares Palace in Seville, dated between the first and second century AD. The chemical composition of pigments is responsible for the colour of the paintings (Edreira *et al.* 2001; 2003). The wood of these Iranian historical building with fantastic architecture are called *Saghatalar* which are specially located in the north of Iran (Mazandaran province) and firstly it was used as a local building as watchtower for agriculture forms. After one and half century, innovation, employing a professional manual activation and best architecture arts on that, their application were changed to religion and holy place in order to do the solemnize rite at MOHARRAM time. The used wood in this historical building is a local tree by name of *Zelkova carpinifolia* with high density and hardness characterization. For this question it is mentionable that the wood of this building is very hard and has a high density to be resistance in climate condition specially humidify and rainy whether of north of Iran. But it could a good layer for conservation and restoration of the wood. The painting on the wood has an invaluable message of the culture and the style of life of the people from the north of Iran. There is another *Saghatalar* that showed the life style and culture of the local people. This study attempts to establish an appropriate methodology for the complete characterization of the pigments by combining portable UV–Visible-FORS and XRF-XRD portable equipment. As far as we know, this is the first study to combine the use of UV–Visible-FORS and XRD portable equipment to analysis mural paintings.

Materials and Methods

The all reagents and solvents were purchased from Merck and used without further purification. Sampling in historical objects and buildings is one of the most sensitive parts in starting research work in the field of cultural heritage and sampling should be as little as possible and with the least damage on the object or monument. All works were carried out at room temperature in air.

Infra-red spectra were obtained on a Nicolet 510P FT-IR spectrometer. Scanning electron microscopies were performed on a Philips XL-300 instrument. UV-Vis spectrophotometric analysis was obtained on the Aventes UV4200 Avaspec spectrometer with Drift accessory. The morphology of wood sample was determined by the field emission scanning electron microscopy (Mira 3-XMU FESEM, Tescan Co, Brno, Czech Republic). The crystalline structure of wood sample was characterized by X-ray diffraction (XRD) analysis at room temperature using a Holland Philips Xpert X-ray powder diffractometer.

Preparing the Colour Samples

The acetone solvent was used for removing the sample colour with the appropriate technique. Therefore impregnating a small amount of cotton (2 g) by acetone and mechanically applied on the desired colour several times and the colour is separated from the wood as shown in the Fig. 1.

a) b)

Figure 1. a) Perspective of roof structure of *Saghatalar*, b) pigment wood samples.

The colour enters the cotton villi, in which the mineral pigments sample can be removed from the cotton by beating or re-dipping with solvent. In the step, the sample of mineral pigments can be removed from the cotton by beating or re-washing with immersion solvent. However, depending on the type of adhesive and substrate used, different solvents such as acetone (C_3H_6O), tetrahydrofuran (C_4H_8O), ethyl acetate ($C_4H_8O_2$) or paraloid can be used.

Results and Discussion

Pigments were first identified by means of XRF analysis according to the X-ray characteristic energies (keV) in each spectrum, corresponding to specific chemical elements. Attribution of different pigments is based on previous consideration from literature (Augelli *et al.* 2007). FT-Raman spectra provided more information on the pigments, while FTIR spectra gave more information on the organic content of painting.

FTIR of Pigments

According to previous studies, having a peak in the specified points in the FTIR spectrum in the Fig. 2 is related to artificial azure blue. Absorption bands in the 1020 cm^{-1} show the indicator peaks related to the azure colour. Other absorption bands in 1383 and 873 cm^{-1} are related to calcium carbonate ($CaCO_3$). The peaks with the numbers 603, 673 and 1113 cm^{-1} are related to the absorption index (gypsum or gypsum plaster). It should be noted that most of the dyes used in *Saghatalars* are associated with a mixture of oils and generally have organic esters carbonyl functional groups and appear in 1730 cm^{-1}. In this sample, because it was first washed with acetone and methanol in the preparation process and most of the esterified oily substances were removed, practically no carbonyl functional group is seen in the IR structure (Fig. 2). In the area above 3000 cm^{-1}, it shows the spectra of organic compounds in the pigment mixture as well as the wood texture introduced into the sample unintentionally during sampling (http://lisa.chem.ut.ee/IR_spectra/paint/pigments/lapis-lazuli). The next pigment tested in this structure is red pigment, which has slightly decreased in colour and has the IR spectrum as follows and in the IR spectrum, the index peaks represent the red colour (Ochre). In the FTIR spectrum, most indicators are related to the Ochre red, which also shows the peak of oils and associated adhesives in the carbonyl ester group at 1730 cm^{-1}. In this case, it has iron oxide compounds with the formula Fe_2O_3 with a high percentage and also a lower percentage of Pb_3O_4, which is attributed to the Ochre Red. The FTIR spectrum of green pigments in the range of 3000 and above has become a wide and indistinct peak, which has made detection a little difficult. The wide peak of the 3327 cm^{-1} region shows most of the hydroxy functional groups that entered the sample from the wood texture at the time of sampling (http://lisa.chem.ut.ee/IR_ spectra/paint/pigments/red-ochre-from-south-estonia, http://lisa.chem.ut.ee/IR_spectra/paint/pigments/italian-gold-ochre-light).

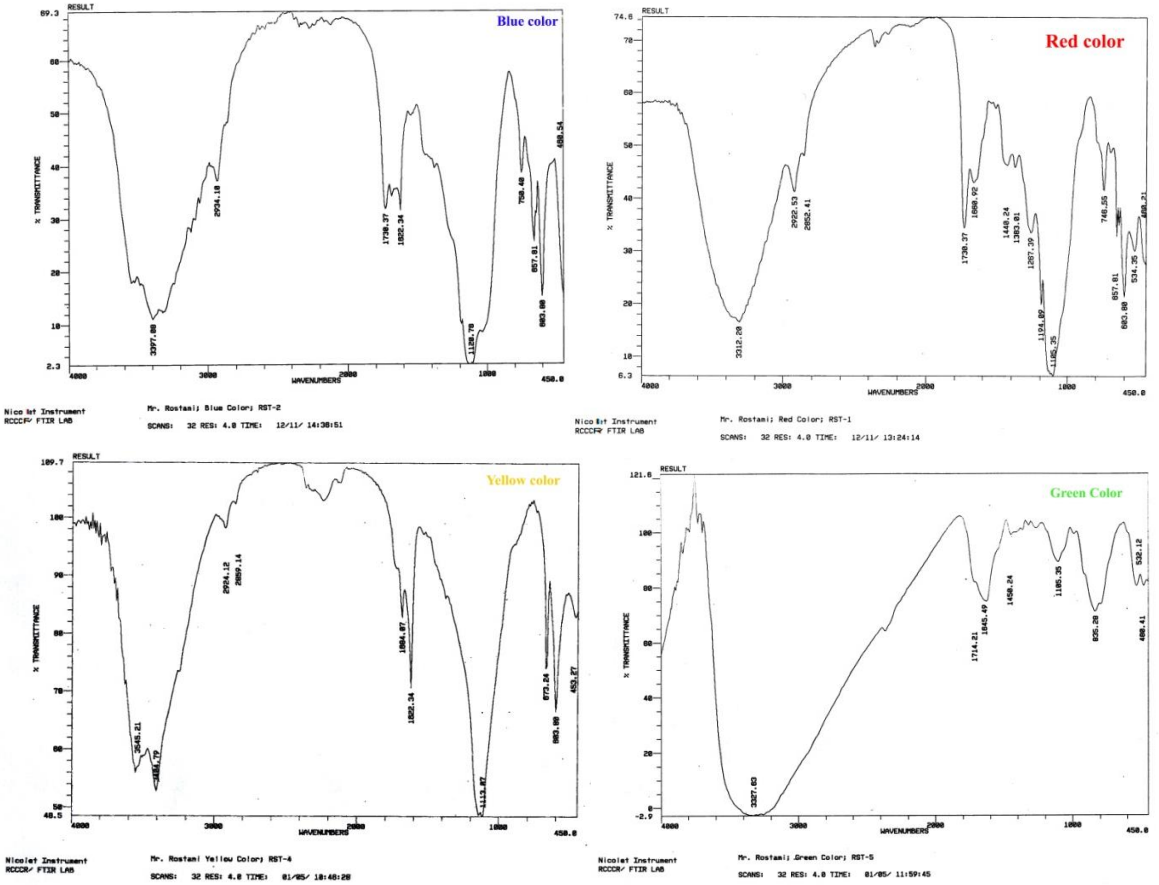
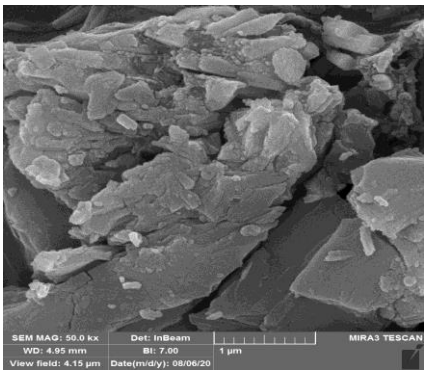


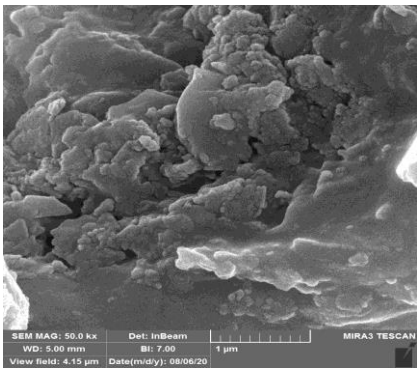
Figure 2. The IR spectrum of pigments.

SEM Images of Pigments

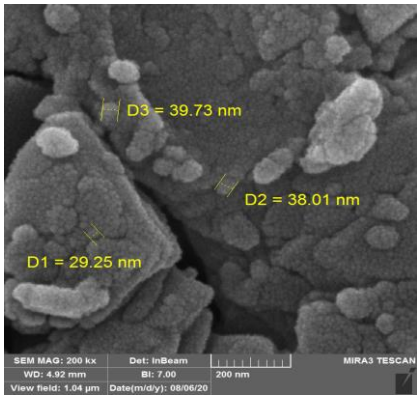
The morphological features of commercial pigments were investigated by scanning electron microscopy (Fig. 3). The SEM micrographs revealed that particles of each pigment are differently shaped and of unequal size (from tens to hundreds microns). The representative SEM micrograph of four colour of *Saghatalar* wood sample is given in Fig. 3.



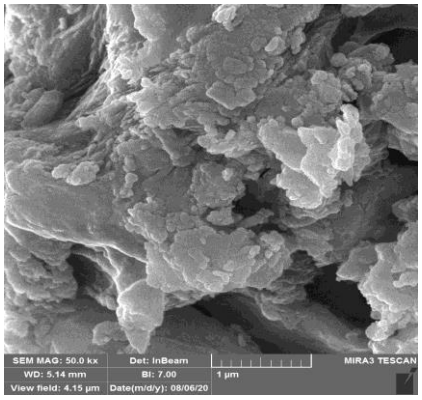
SEM image of blue color



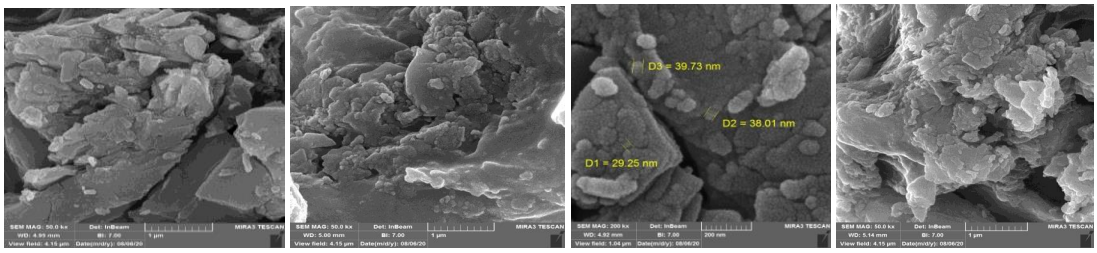
SEM image of red color



SEM image of yellow color



SEM image of green color



Blue Red Yellow Green

Figure 3. SEM image of pigments.

EDX Analysis of Pigments

Elemental analysis of the wood samples was performed using EDX technique (Fig. 4). As shown in Fig. 4, Cr, Fe, O, C, Mg, Cu and Si show the elements in the wood sample.

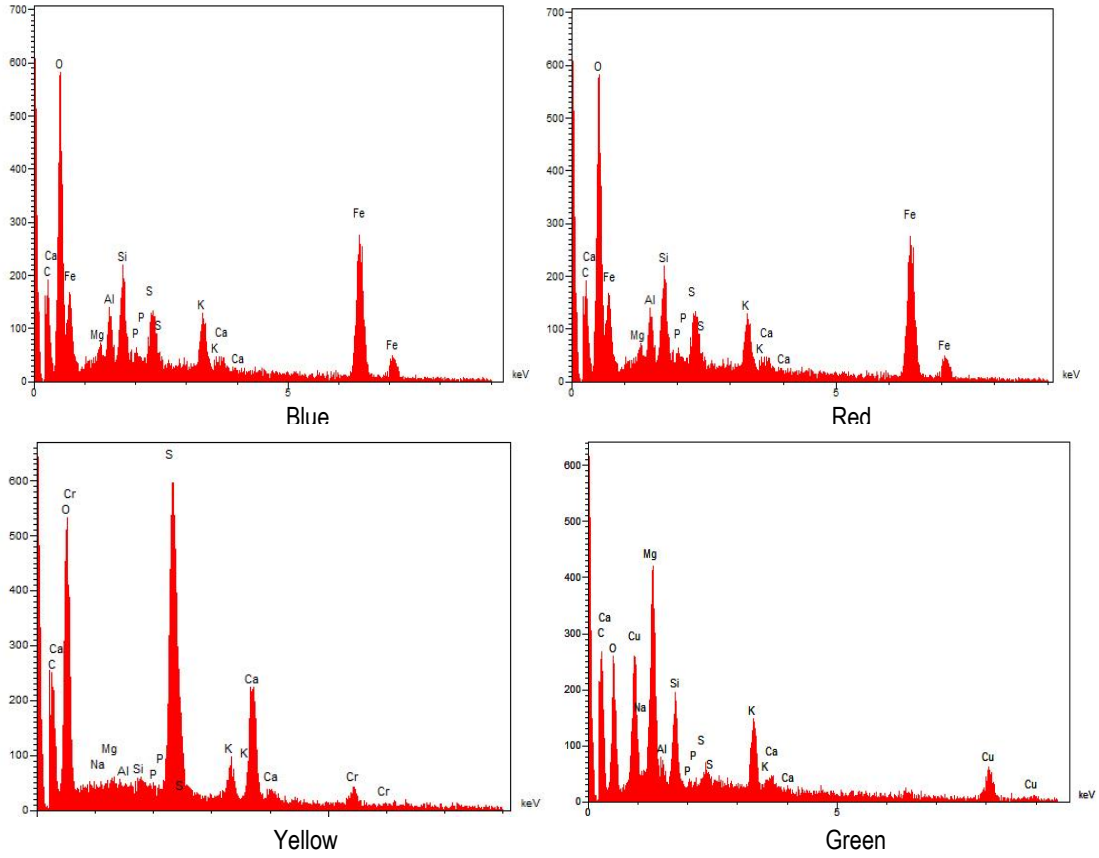


Figure 4. EDX analysis of wood samples.

XRD Analysis of Pigments

Some of the most significant phases in these pigments in XRD show as a separate phase (Fig. 5). The sharp expression of calcium sulfate is gypsum. Therefore, because the amount of gypsum has a high percentage in the pigment mixture, which often shows sharper, peaks than the pigment. However, in the list of resulting peaks, in addition to gypsum, whose standard diagram is shown at the bottom of the diagram, the main peak has other peaks that are related to the structure of the main pigment and gypsum impurities.

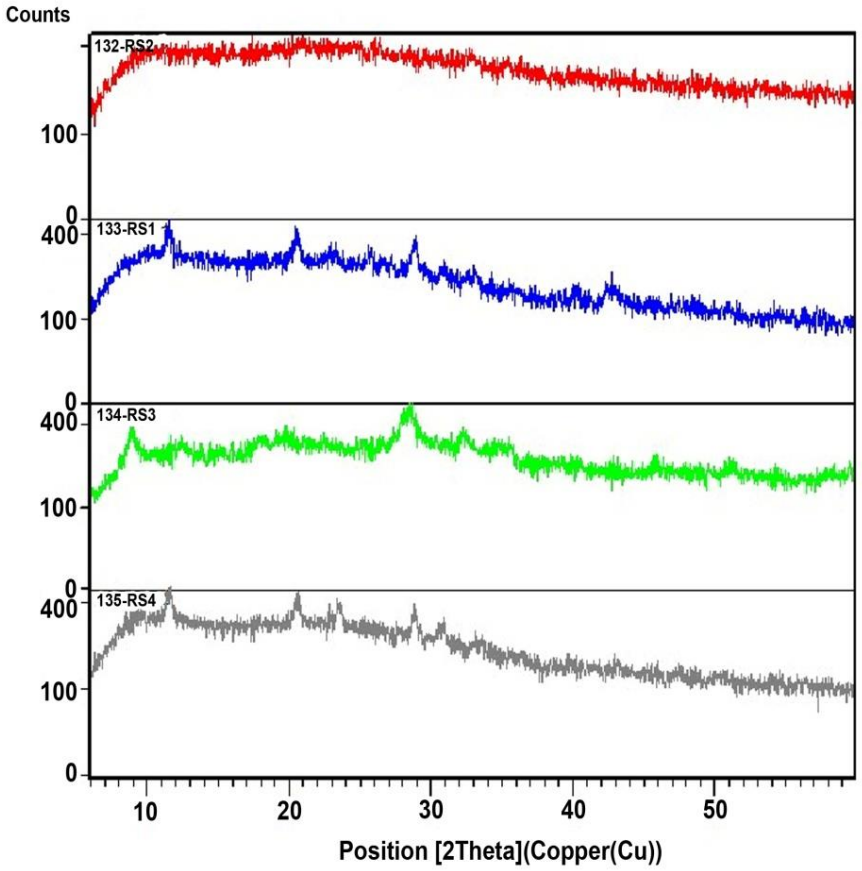


Figure 5. XRD analysis of four pigments in *Saghatalar* sample.

XRF Analysis of Pigments

In elemental analysis in XRF spectrum, the following items have been shown as the results of this spectroscopy and according to the formula of azure pigment Blue azurite $(NaCa)_8$ $[(SO_4SCl)$ - $(AlSiO_4)_6]$ and also in the composition of Blue amulet which are located on the wooden elements the following elements and compounds can be identified (Fig. 6). Indicative elements in this XRF spectrum are calcium 19.15%, potassium 17.99% and sulfur with 21.76% and silicon with 4.7% and it also has a lot of structural similarity compared to the standard azure blue spectrum (Standard IR-Spectra web address of Pigments) and is also decisive with other analysis results such as p-XRF and more chemical testing with acid and H_2S gas release. The chemical structure of this blue dye is confirmed by synthetic azure blue. According to the table below, the percentage of silicon, aluminum, and sulfur compounds in the blue pigment using elemental analysis can indicate the presence of artificial azure pigment as additional information.

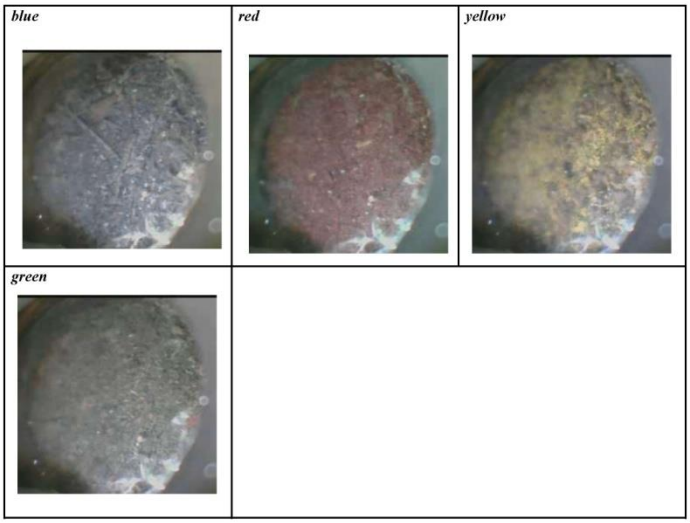


Figure 6. Four pigments in *Saghatalar* sample.

Table 1: XRF analysis of four pigments in *Saghatalar* sample

	Blue	Red	Yellow	Green	Tape
Sample	(%)				
Bal	30.83	43.23	40.482	48.903	66.045
Al	1.661	0.934	0.593	0.712	1.807
Si	4.759	3.534	4.124	2.296	9.964
P	0.43	0.506	0.541	0.275	1.189
S	21.76	8.421	20.683	4.501	12.750
Cl	0.73	0.478	0.859	0.590	2.303
K	17.99	7.541	2.463	4.490	-
Ca	19.18	2.478	24.588	2.873	1.983
Ti	0.21	0.102	-	0.031	0.048
Cr	0.02	0.070	1.063	-	-
Mn	-	-	0.164	0.034	-
Fe	1.24	30.817	1.450	0.35	0.25
Cu	0.76	0.655	0.669	18.322	1.175
Zn	0.02	0.293	0.029	-	-
Ba	0.02	0.024	0.323	0.016	0.039
As	0.09	0.532	0.433	16.387	0.009
Pb	0.19	0.301	1.477	0.179	0.007

The XRF analysis results of these four colours are summarized in the above Table 1. The Niton XL3t GOLDD + 950 portable XRF portable fluorescence spectroscopy device is of Thermo Scientific handheld portable type. It is noteworthy that the sample witnessed the book adhesive to which the colour powder of the four samples adhered and acted as a retaining substrate, and since it lacks mineral compounds, it is mainly organic compounds and has shown the least disturbance in the analysis.

Petrography Investigation of Four Colours

In this study, 4 samples of blue, red, yellow and green pigments obtained from *Saghatalars* have been analyzed and necessary. In this microscopic study (Fig. 7), the magnification of the device is 10x and observations have been made in polarized and cross-polarized light (XPL).

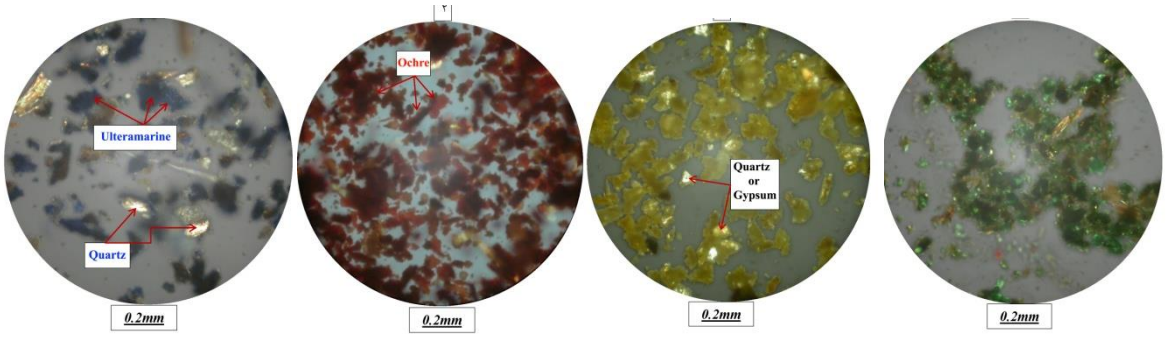


Figure 7. Petrography of four colours.

The details of the results obtained from petrography of blue pigment petrography are as follows. Or artificial azure has been identified by the chemical formula of the mineral lapis lazuli (Na_8 [$Al_6Si_6O_{24}$] Sn). Impurities are seen in the pigment. Finally, by microscopic examination of the red pigment, observing a high percentage of the target pigment, the "ochre" pigment is the most likely. The probable composition identified in the XRD analysis is gypsum, but its yellow colour can be attributed to a mixture of lead and iron oxide according to the XRF and FTIR results. Its microscopic studies also show cases such as quartz and gypsum.

Conclusions

In this study, In order to summarize the results obtained from the analyzes performed by FTIR, XRF, XRD and cross-sectional area and microscopic photographs in the petrographic laboratory on four categories of pigments extracted from the small woodpecker of Fereydunkenar neighborhood, the pigments used from. They were made of minerals and also organic materials such as gums and natural resins were used to fix the colour on the wood. Sometimes gypsum has been used to create a uniform composition with higher adhesion. The following results have been obtained by interpreting the spectra and data obtained from multiple analyzes obtained from FTIR, p-XRF, XRD and cross-sectional area and microscopic images of pigments extracted from the studied sciatica. Synthetic azure blue pigment with quartz crystals Blue azurite $(NaCa)_8$ $[(SO_4SCl)$ - $(AlSiO_4)_6]$, and ocher red pigment ocher $FexO_3$ and yellow composite Chromium yellow ($PbCrO_4$) is attributed to $PbSO_4$ lead sulfate as well as Scheele's Green ($CuHAsO_3$) green pigment. Of course, it should be noted that blue, red and yellow pigments and ester compounds of gum and resin can also be seen in the pigment. On the other hand, green and yellow colours in FTIR and XRD analyzes do not have good resolution and the peaks do not appear clearly and the most confirmation of its structure is based on XRF, which requires more professional analysis with EDX and SEM is that the necessary results can be obtained by comparing with references.

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