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Imane Fikri, Mohamed El Amraoui, Mustapha Haddad, Ahmed Saleh Ettahiri, Ludovic Bellot-Gurlet, et al.. XRF and UV-Vis-NIR analyses of medieval wall paintings of al-Qarawiyyin Mosque (Morocco). IOP Conference Series: Materials Science and Engineering, 2018, 353, pp.012020. 10.1088/1757-899X/353/1/012020. hal-01797342

HAL Id: hal-01797342

<https://hal.science/hal-01797342>

Submitted on 22 May 2018

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To cite this article: I Fikri *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **353** 012020

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XRF and UV-Vis-NIR analyses of medieval wall paintings of al-Qarawiyyin Mosque (Morocco)

I Fikri¹, M El Amraoui¹, M Haddad¹, A S Ettahiri², L Bellot-Gurlet³,
C Falguères⁴, M Lebon⁴, R Nespoulet⁴, S Ait Lyazidi¹, L Bejjit¹

¹Laboratoire de Spectrométrie des Matériaux et Archéomatériaux (LASMAR), URAC11, Faculté des Sciences, Meknès, Université Moulay Ismail (Maroc)

²Institut National des Sciences de l'Archéologie et du Patrimoine (INSAP), Rabat (Maroc)

³MONARIS, UMR 8233, Université Pierre et Marie Curie, Paris (France)

⁴Muséum National d'Histoire Naturelle, UMR7194, Paris (France)

Email: mhaddad22@yahoo.fr

Abstract. Medieval wall painting fragments, taken at the medieval Mosque of al-Qarawiyyin in Fez, have been investigated by means of X-ray fluorescence and UV-Vis-NIR diffuse reflectance spectroscopies. The analyses permitted to determine the palette of pigments used by craftsmen of the time. Hematite or red ochre were used to obtain red brown colours, calcite for white, copper-based pigments for blue and blue-grey shades while a mixture of cinnabar, lead-based pigments and hematite was adopted to make red-orange colours. Furthermore, the analysis of mortars (external layer and plaster) on these wall painting samples revealed that they are composed mainly by calcite and sometimes by additional compounds such as quartz and gypsum.

1. Introduction

In the recent decade, there has been a great interest in the use of non-invasive analytical techniques able to answer specific questions about materials used in handcrafting of ancient artworks, for conservation sciences, archaeological studies and art history goals [1-3]. The present work relates to medieval wall paintings, dating back to the 11th-12th centuries, at the al-Qarawiyyin Mosque of Fez. The Mosque al-Qarawiyyin, funded in the 9th century, is the oldest university in the Islamic world. Most studies conducted on Islamic wall paintings deal with those in Spain [2,4-7]; none study concerned those of Morocco.

Numerous wall paintings fragments, originating from al-Qarawiyyin Mosque, are investigated by mean of combining elementary and structural analyses in order to characterize painting and mortar layers. The adopted techniques are X-ray fluorescence and UV-Vis-NIR diffuse reflectance spectroscopies; both are non-invasive, not requiring any material removing from the painting surface. X-ray fluorescence permits elementary analyses identifying chemical elements in inorganic materials [8], while UV-Vis-NIR diffuse reflectance allows structural analyses of pigments [9-13] and colourants with a high degree of probability [14].

The wall painting fragments were collected in the course of a recent excavation in al-Qarawiyyin architectural site. They might originate from two neighbouring houses demolished during the extension of the mosque in 1134, during the Almoravids Dynasty period. Only results relating to six representative fragments are shown.

The work is part of a research project aiming to find more information to differentiate between materials and handcrafting techniques adopted in Mediterranean sites. The results will also enlarge an



ongoing database on ancient Moroccan wall paintings from the Roman period (Banasa and Volubilis sites) to the medieval Islamic one.

2. Materials and Techniques

2.1. Materials

Six representative wall painting fragments (figure 1), among a large set of pieces dating back to the 11th -12th century period taken at al-Qarawiyyin Mosque, were studied. The samples exhibit different colourful decorative patterns designed on mortar surfaces. They are of irregular sizes varying from 4 cm x 4 cm to 17 cm x 6 cm, with thicknesses in the range 1 to 3 cm.

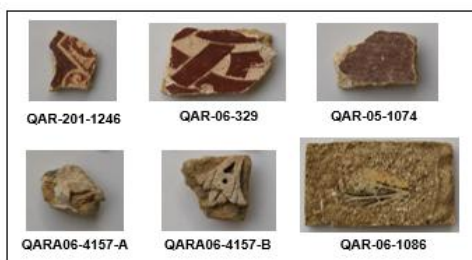


Figure 1. Photographs of the wall painting studied samples

The six fragments are referenced QAR-201-1246, QAR-06-329, QAR-05-1074, QAR-06-1086, QARA06-4157-A and QARA06-4157-B. On the basis of careful macroscopic observations, the two first pieces show dichromatic decorations in white and dark red-brown shades, the third one appears as a dark red-brown monochromatic surface, the fourth fragment presents red-orange and blue-grey areas isolated by thin black strips, while the fifth and sixth ones look like carved mortars with small areas of faint blue pigmentation. The patterns colours are applied on white or yellowish layers of mortars, with very fine aggregates.

2.2. Techniques

All reflectance spectra were recorded on a JASCO V-570 UV-Vis-NIR spectrometer equipped with an integrating sphere; the reference is a BaSO₄ tick plaque. All measures are repeated several times upon varying the spotted zone on the fragment surface. Pigments identification was achieved by mean of reflectance spectra databases [15].

XRF elementary analyses were carried out on an ELIO portable energy dispersive spectrometer managed by XG ELIO software, highly sensitive in the full range 1–40 keV. The X-ray source is a tube of Rh-anode operating at maximum (40 kV - 200 μ A). The spectra were measured on spots of 0.25 mm² size area during 300 seconds. The instrument has a resolution lower than 140 eV at line peak $K\alpha$ 5.9 keV of Manganese. Chemical elements were identified on the basis of their characteristic X-ray peaks energies [1].

3. Results and discussion

Figure 2 shows the XRF spectra recorded on all fragments. The main elements detected in these samples are calcium (Ca), iron (Fe), copper (Cu), mercury (Hg), sulfur (S); and lead (Pb). To complete this qualitative analysis by a structural one, UV-Vis-NIR spectra were recorded.

3.1. Red-brown and white paintings

Only the three red-brown colour samples referenced QAR-05-1074, QAR-201-1246 and QAR-06-329 have been analysed by optical reflectance spectrometry (figure 3); it was not possible to analyse the other fragments because of their dimensions and their geometrical. All red-brown areas show similar spectra exhibiting their maximum at 740 nm and characterized by a sharp positive slope between 550 and 600 nm. A strong absorption band around 490 nm along with another weak one in the near infrared 840-870 nm side are also observed. These latter bands are attributed to electronic transitions of Fe³⁺ ions [16-19]. This is in accordance with the red-brown's reflectance spectrum first derivative (figure 3 FD) which shows an inflexion point around 585 nm characteristic of iron Fe³⁺. From these results, it seems that red ochre or hematite (α -Fe₂O₃) had been used to achieve the red-brown colour

[3,16,20,21]. XRF spectra (figure 2.I-a,b,c) support then this finding; they revealed Iron (Fe) and Calcium (Ca) as principal chemical elements, detected in high content, in the red-brown areas of samples QAR-05-1074, QAR-06-329 and QAR-201-1246. Hematite used to be preferred as a red pigment since antiquity because of its availability, easy preparation and also low cost. Its deep colour gives an exceptional contrast with white backgrounds promoting thus the visual effect, such as the case of the present dichromatic samples [5].

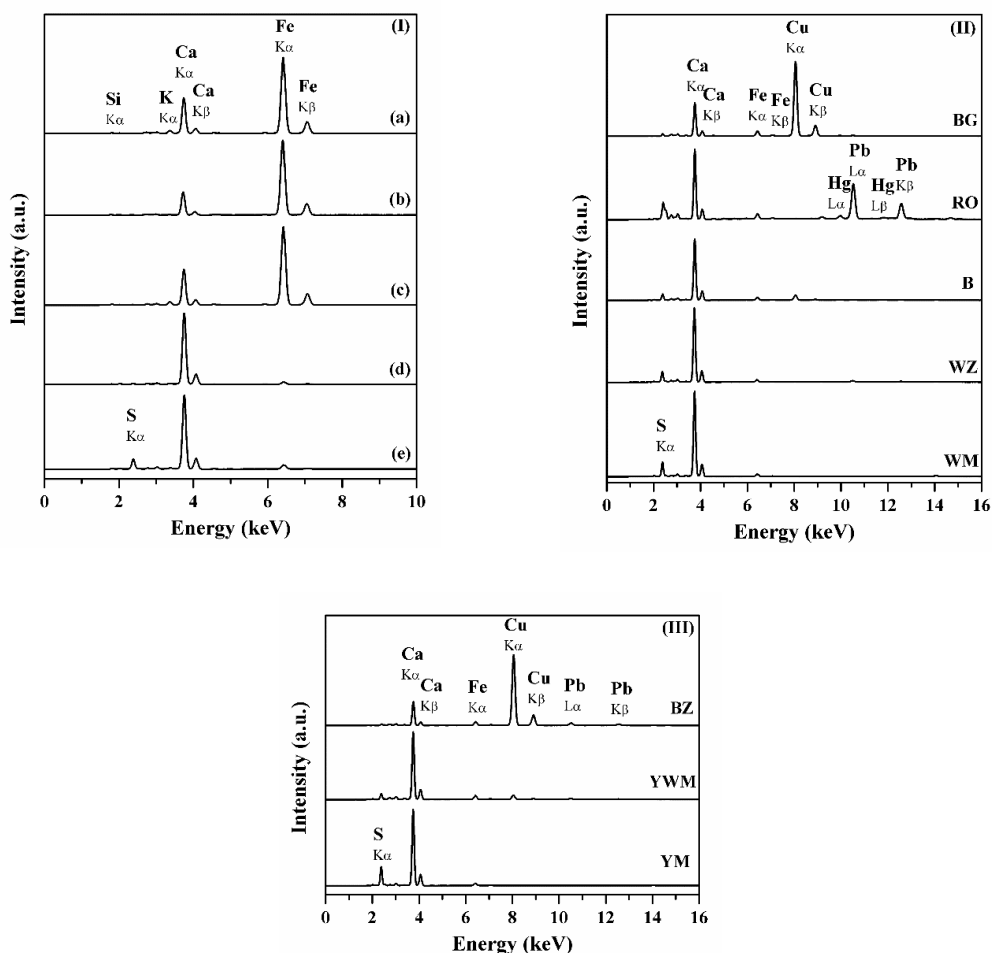


Figure 2. XRF spectra

(I) Dark red-brown areas in samples QAR-05-1074 (a), QAR-201-1246 (b) and QAR-06-329 (c); white zone (d) and white mortar (e) in sample QAR-06-329.

(II) Blue grey (BG), red orange (RO), black (B), white zone (WZ) and white mortar (WM) in sample QAR-06-1086.

(III) Blue zone (BZ), yellowish white (YWM) and white (YM) mortars in sample QARA06-4157-A.

On all reflectance spectra there are three additional absorption bands observed around 1450, 1740 and 1950 nm which can be associated to natural gypsum (calcium sulfate dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) [18,22], or to carbonate ion CO_3^{2-} resulting from the presence of calcite (CaCO_3) in the red-brown areas [18]. The observed high relative intensity of calcium in white zones (figure 2) is indicative of using calcite (CaCO_3); calcite used to be adopted to produce white colours [16,23]. Calcite has been also revealed by Raman measurements (results to be published). Calcium is also present in all samples areas; it was likely used either as a principal component to achieve under layer (called intonaco) of paintings or as a shade lightening.

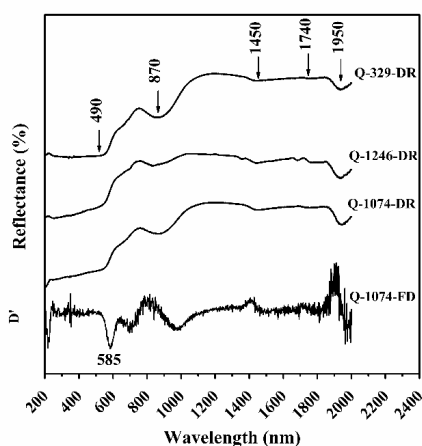


Figure 3. Reflectance spectra of dark red-brown colour areas (DR) in samples QAR-06-329, QAR-201-1246 and QAR-05-1074; diffuse reflectance first derivative spectrum (FD) of QAR-05-1074 (bottom).

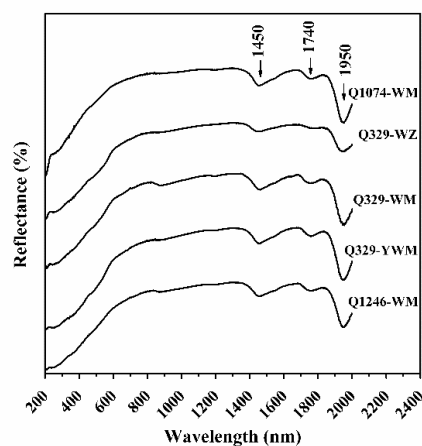


Figure 4. Reflectance spectra of white mortar (WM) in fragment QAR-05-1074; white zone (WZ), white mortar (WM) and yellowish white mortar (YWM) in fragment QAR-06-329 and white mortar (WM) in fragment QAR-201-1246.

3.2. Blue colour painting

XRF measured on the blue colour areas of samples QARA06-4157-A and QARA06-4157-B are shown in (figure 2.III-BZ). The analyses highlight the presence of copper (Cu) in high content. This element points out that a Cu-based pigment was used to achieve the blue colour of the painting, Raman measurements have been used in this case to specify the identity of the Cu-based pigment which is Azurite [$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$] (results to be published). Calcium (Ca), iron (Fe) and lead (Pb) are also observed in all blue areas. As underlined above, neither the dimensions nor the geometrical 3D-forms of these fragments permitted UV-Vis-NIR diffuse reflectance measurements on them.

3.3. Polychrome painting

XRF measurements recorded on red-orange areas of sample QAR-06-1086 (figure 2.II-RO) revealed Lead (Pb), mercury (Hg), sulfur (S) and calcium (Ca) as principal chemical elements in this painting. The presence of these chemical elements suggests that a mixture of mercuric sulphide (HgS) and a Pb-based pigment such as minium (Pb_3O_4) was adopted to obtain the red-orange colour [13,17,25]. Iron (Fe) is also present in a low amount, this refers to hematite ($\alpha\text{-Fe}_2\text{O}_3$) or red ochre both containing iron (Fe). Therefore, all the pigments, minium, cinnabar or vermilion, hematite and/or red ochre were used to produce the red-orange colour.

Copper (Cu) is the principal chemical element identified by XRF measurements in the blue-grey areas of QAR-06-1086 polychrome sample (figure 2.II-BG). This result points out that a copper-based blue pigment such as Azurite [$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$] or Egyptian blue had been used [21]. For black areas on the fragment the XRF spectra didn't indicate any elements which could be related to the black colour. Consequently, black paintings were very likely realized by means of an organic compounds-based receipt such as carbon black or ivory whose chemical elements cannot be seen in XRF spectra [1, 11].

3.4. Mortars

XRF spectra measured on mortars layers (figures 2. I-e, 2.II-WM and 2.III-WM) show high amounts of calcium (Ca) with relatively lower amounts of sulfur (S). This result suggests that calcite (CaCO_3) was the principal component in the present mortars [17,26]. This is consistent with UV-Vis-NIR reflectance measurements (figure 4) revealing bands attributable to calcium sulphate dehydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Quartz is also highlighted in these materials indicating thus that sand was likely used with white lime (calcite) to produce layers of plasters.

4. Conclusion

A set of six representative wall painting fragments, chosen among a large series of pieces sampled at the medieval al-Qarawiyyin Mosque of Fez, have been characterized by mean of crossing elementary XRF analyses and structural UV-Vis-NIR diffuse reflectance spectrometry techniques. The adopted colouring materials in these paintings have been identified and characterized.

The measurements revealed that: i) red-orange shades are mainly lead-based pigments types with additional cinnabar and traces of hematite or red ochre, ii) red-brown colours had been achieved by hematite or red ochre mixed with some amounts of black pigments, iii) blue and blue-grey colours are copper-based pigments, while vi) calcite used to be adopted to make white colour of painting layers. The investigations showed also that mortars of wall paintings are composed principally of calcite with minor amount of gypsum.

The identified palette of painting materials used to be adopted by craftsmen of the period seems likely arranged by local and imported pigments. These results are of great importance while choosing painting materials for future restoring operations.

Acknowledgments

This study was supported by Moroccan CNRST and French CNRS, and by ColorHOM project.

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