

Spectrometric Characterization of Moroccan Architectural Glazed Tiles

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Abstract The present work relates to a multi-analytic characterization of glazed tiles consisting of green monochrome glazed ceramics used in Moroccan architecture to protect ceilings, walls and roofs from rainwater. These tiles originate from five sites and date back to different historical periods: Bou-Inania Madrasa in Meknes (14th century), Prison of Qara in Meknes (18th century), Dar El-Beida Palace in Meknes (18th century) and Al-Hibous Cemetery of Mdaghra in Errachidia (19th century). Different analysis techniques were used in view to go back to the ancient technological processes adopted (materials, coloring pigments, firing temperatures, etc.). Optical absorption spectrometry revealed two different types of chromogenic ions in green glazes, chromium Cr³⁺ in the case of the tiles from Dar El-Beida Palace and Prison of Qara, and copper Cu²⁺ in the case of the tiles from Bou-Inania Madrasa and Al-Hibous Cemetery. Raman microspectroscopy identified different coloring phases with two types of green glazes, esolaite (Cr₂O₃) in the case of the glazes of the Prison of Qara and copper phthalocyanine mixed with a chromium-based pigment in the case of the glazes of the Dar El-Beida Palace. However, the origin of the green color in the glazes from Bou-Inania Medersa in Meknes and Al-Hibous cemetery of Errachidia may be due to the dissolution of copper in the vitreous glazes. X-ray diffraction, supported by Raman microspectrometry, revealed the mineralogical compositions of the terracotta tiles. Quartz and calcite are the main phases, while hematite and "high temperature" phases (anorthite, gehlenite and diopside) appear as minority ones. These identified phases permit to estimate the firing temperature of the tiles at around 950 °C in an oxidizing atmosphere. The chromatic coordinates of all glazes, represented in the Lab CIE color space, made it possible to discriminate objectively all green colors. The present investigation of glazes from different historical sites allowed the exploration of the coloring materials, revealed differences in the adopted technological protocols and permitted the establishment of a color reference database to follow glazes degradation and to help while replacing missing or degraded tile pieces.

1. Introduction

Several cities in Morocco conceal a very rich and diversified historical architectural heritage. Meknes city in particular, founded in the 11th century by the Almoravids as a military settlement and becoming a capital under Sultan Moulay Ismaïl (1672–1727), has several monuments and sites in good state : Madrasa Bou-Inania, Madrasa Filalia, Palace Dar-El Beïda, Palace Al Mansour, Sultan Moulay Ismaïl Mausoleum, Quara Prison, portals Bab Al Mansour Laalaj, Bab Al Khmis, Bab Berdaine, ramparts, fountains, Kasbahs. This architectural heritage is recognized worldwide, for example, the old medina of Meknes (Lahdim) has been classified since 1996, as an UNESCO World Heritage Site. Several types of building materials were served as part of this architectural

heritage. Among these materials, Moroccan glazed ceramic called (Zelliges or zellij), roofing glazed tiles called (Quermoud), wall paintings, plasters, gypsum, carved wood and painted wood are used in architectural decoration and the protection of monuments. For most monuments in Meknes, studies on Moroccan glazed ceramics (zellige) as decorative and protective materials, have been carried out [1-7]. But studies of roofing glazed tiles remain absent. Thus, investigations of especially Moroccan glazed roofing tiles “Quermoud” are necessary, because several of them, in most ancient monuments, show degradation, destruction, cracking, flaking and detachment of their glazes. Also, they have lost their impressive image due to weather conditions (rain, wind, sunshine) and pollution.

Green glazed roofing ceramic tile is an architectural element that covers the roofs of Palaces, Mosques, Medersas. A glazed ceramic is a composite material composed by a ceramic support called also terracotta or ceramic body on which a glaze is deposited (enamel, glass) that serves both to waterproof and to decorate it. The main components of a glaze are: silica as vitrifier and network former, fluxes or network modifiers (lead, natron,...), stabilizing oxides, colouring elements (copper, cobalt, iron, manganese,...) and opacifying elements (tin oxide, ...). These glazed roofing tiles are often monochrome green colour.

The presented work is a part of a spectrometric studies project of Moroccan historical architectural glazed ceramics and especially glazed roofing ceramic tiles started many years ago [1-7]. The main objective is to identify the colouring materials and ancient handcrafting techniques adopted to manufacture green glazed roofing tiles of different sites selected. Results presented, in this work, will contribute to create a database of Moroccan architectural glazed roofing tiles, which will be useful for conservation and restoration. Thus, Raman micro-spectrometry, optical reflectance spectroscopy, colorimetry and X-ray diffraction, have been used to characterize samples from sites cited above.

2. Materials and Techniques

2.1 Materials

Samples of green glazed roofing tiles, from four monuments and sites (figure 1), were selected and referenced as: MEK-GGRTMBIM from Madrasa Bou Inania (14th century), MEK-GGRTPDEBM from Dar-El Beïda Palace (18th century), MEK-GGRTQPM from Quara Prison (18th century) in Meknes and MEK-GGRTGHME from Graveyard Hibous Mdaghra (19th century) in Errachidia.



MEK-GGRTMBIM

Interior view, Minaret and sample of Madrasa Bou Inania (Meknes)



MEK-GGRTDEBPM

Sample and view of Dar El-Beida palace (Meknes)



Entrance view of Quara Prison (Meknes)



MEK-GGRTQPM



Sample and view of graveyard Hibous Mdaghra (Errachidia).



MEK-GGRTGHME

Figure 1: Samples and view of sites

2.2 Characterization Techniques

Raman analyses

Raman spectra were recorded using a Renishaw RM1000 spectrometer equipped with a CCD detector and an external Leica DMLM confocal microscope with 5×, 20×, 50× and 100× objectives. The excitation source is a He-Ne laser of wavelength 632.8 nm. The laser beam is focused directly on the sample without any preparation.

Colorimetric and visible measurements

The portable Konica Minolta CM700d spectrophotometer working in the visible wavelength range 400–700 nm with a D65 illuminant, is used for optical and colorimetric measurements. The instrument is provided with its own white reference (100% reflective) and a zero calibration box (0% reference). Data are collected as L*, a* and b* coordinates.

Mineral phase analyses

Powder mineralogical analyses of ceramic bodies were performed using a BRUKER D8 ADVANCE x-ray diffractometer. It is equipped with an x-ray tube with a copper anode (Cu-K_{α1}, λ=1.5406 Å) operating at 40 kV and 30 mA. The position 2θ varies from 5 to 70° with a step of 0.02°. The mineral phases were identified using the Ruff database [8].

3. Results and discussion

3.1 Colorimetric coordinates

Table 1 presents the chromatic coordinates of the four studied glazes in (L, a*, b*) space and figure 2 show their presentation in (a*, b*) diagram. According to the chromatic (a*, b*) space, we can notice that the chromatic coordinates of the green glazes are located in the dial placed between the green axis (- a*) and the yellow axis (b*) i.e. the green-yellow dial. The chromatic coordinates of samples MEK-GGRTMBIM, MEK-GGRTGHME and MEK-GGRTQPM present a significant contribution to green colour than yellow, unlike that of MEK-GGRTDEBM sample which presents a significant contribution of yellow than green colour.

Table 1: chromatic coordinates of glazes of samples in (L, a, b*) space*

Samples	L*	a*	b*
MEK-GGRTMBIM	46.34	-16.23	5.33
MEK-GGRTDEBM	43.91	-4.96	14.49
MEK-GGRTQPM	37.44	-12.58	12.66
MEK-GGRTGHME	33.78	-9.27	8.11

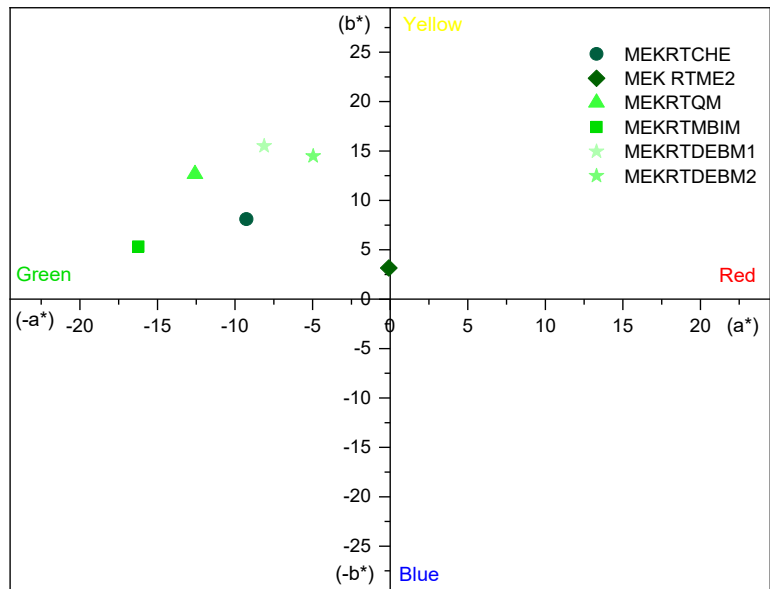


Figure 2: chromatic coordinates of green glazes studied in (a*, b*) space

3.2 Optical reflectance spectrometry

Figure 3 presents the optical reflectance spectra of green glazes of samples MEK-GGRTMBIM and MEK-GGRTGHME. The spectra show the presence of a broad band centred at 520 nm which can be attributed to copper-ions Cu^{2+} . These ions are responsible of the green colour of glazes of ceramic tiles [6; 9].

The optical reflectance spectra of green glazes of MEK-GGRTDEBM and MEK-GGRTQPM samples are presented in figure 4. They show the presence of two bands centred at 410 and 540 nm. These bands are characteristic of d-d electronic transitions of chromium ions Cr^{3+} in an octahedral site in a vitreous matrix. It is well known that the chromium ions are responsible of the green colour of glazes of ceramic tiles [6; 9].

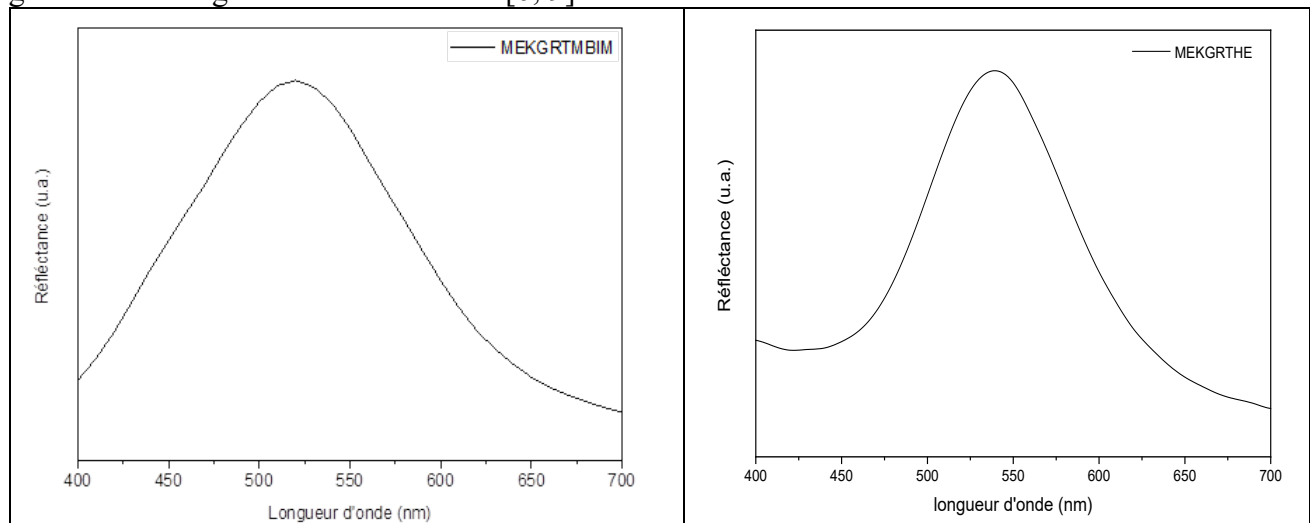


Figure 3: optical reflectance spectra of green glazes of MEK-GGRTMBIM and MEK-GGRTGHME

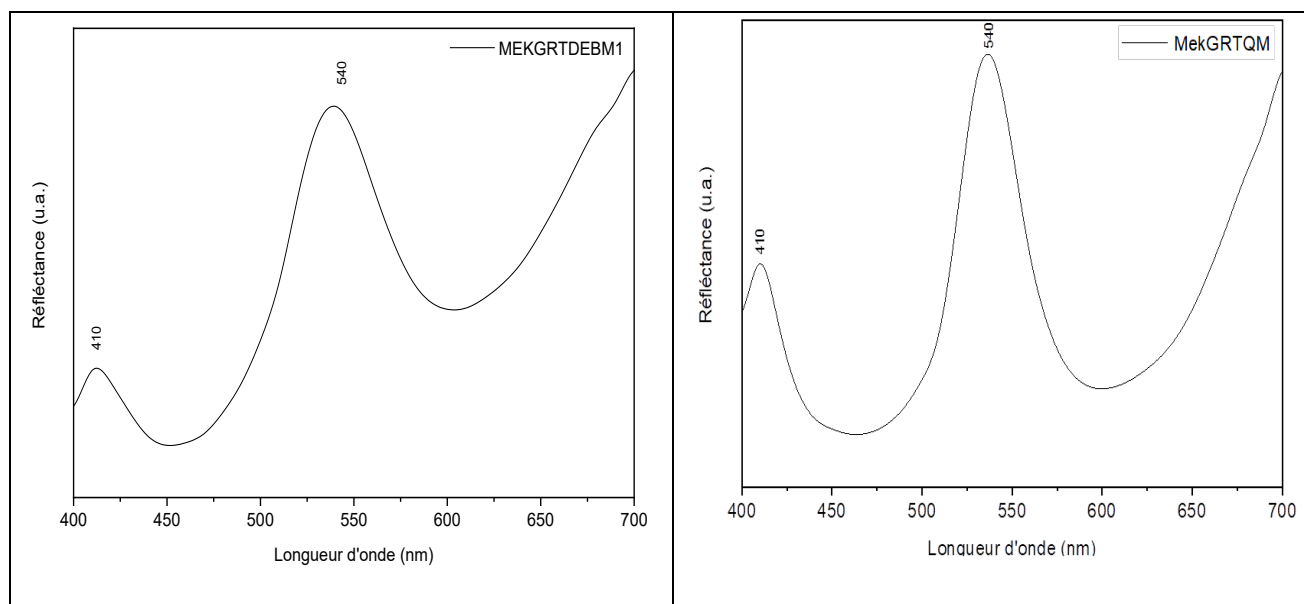


Figure 4: optical reflectance spectra of green glazes of MEK-GGRTDEBM and MEK-GGRTQM

3.3 Raman spectrometry of glazes

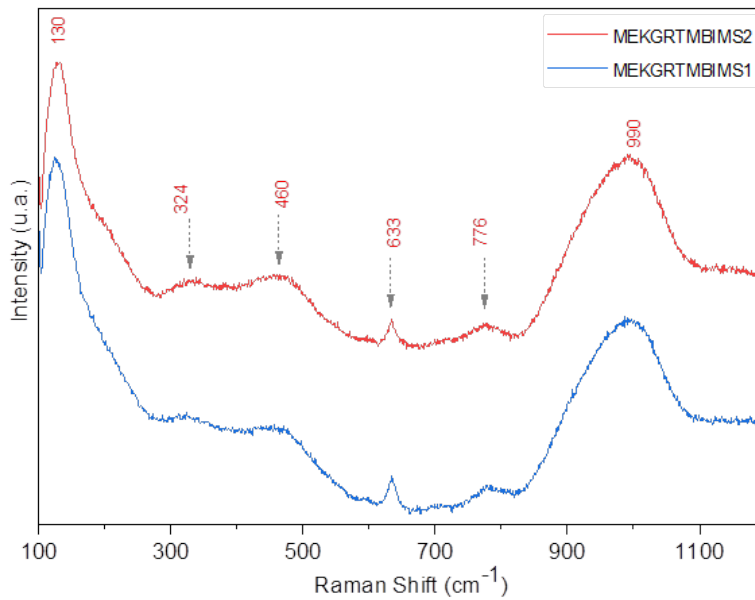
Figure 5 presents the Raman spectra recorded on different areas of the green glaze of the sample MEK-GGRTMBIM. These spectra generally show the same bands: 130; 324; 460; 633; 776 and 990 cm^{-1} . Bands at 460 and 990 cm^{-1} are characteristic of silicate glasses [5; 6; 10; 11; 12]. The first band located at 460 cm^{-1} corresponds to the bending modes of the SiO_4 tetrahedral, especially, to the displacement of the bridging oxygen along the line bisecting the Si-O-Si angle. The second band located at 990 cm^{-1} corresponds to the Si-O stretching vibrations in the silicates glasses [5; 6; 7; 10; 11; 12]. This band is generally located at 1000 cm^{-1} for silicate glasses and it is shifted towards 990 cm^{-1} which is a Raman signature of lead glazes [6; 7; 10; 15; 16]. This stretching block of Si-O is more intense than that of bending Si-O-Si which indicates strong depolymerisation of the silicate network consistent with a lead-rich glaze composition [15]. The doublet located at 633 and 776 cm^{-1} is a Raman signature of cassiterite a tin oxide (SnO_2) [5; 6; 7; 10; 11-13] used as an opacifier of glazes [5; 6; 7; 10; 11-13]. The bands located around 130 and 324 cm^{-1} can be attributed to lead antimonite also called Naples yellow ($\text{Pb}_2\text{Sb}_2\text{O}_7$) [10;13; 17]. It should be noted that tin oxide and Naples yellow were also used as glaze opacifiers [6; 13].

Although, no colouring phase responsible for the green colour of the glaze is not detected in the spectrum, the green colour of silicates glazes could be due to the dissolution of copper ions Cu^{2+} in a silicate vitreous matrix called transparent glazes [6; 7; 13; 18]. We note that the ions Cu^{2+} are detected by optical absorption spectrometry (figure 3). Therefore, the colour of this green glaze of sample MEK-GGRTMBIM is a copper-based pigment.

Raman Analyse of MEK-GGRTGHME sample presented in figure 6 shows the same bands than MEK-GGRTMBIM except the band at 633 cm^{-1} . Therefore, we can conclude that a copper-based pigment is responsible of the green colour in this glaze since it is generally dissolved in transparent lead glazes [6; 7 ; 13; 18].

Raman spectra recorded on the green glaze of MEK-GGRTDEBM (Figure 7) present several bands: 236, 260, 303, 486, 595, 682, 750, 781, 835, 954, 1011, 1042, 1110, 1143, 1164, 1199, 1217, 1308, 1343, 1433, 1452 and 1531 cm^{-1} . These bands are the Raman signatures of copper phthalocyanine, it is a synthetic organic pigment [19, 20]. As the optical absorption spectroscopy indicated that the chromogenic ions responsible for the green color of the glaze are Cr^{3+} ion, we suggest that the chromium-based pigment is mixed with the identified organic pigment to give the

green colour of this glaze. The absence of the Raman signatures of the chromium-based pigment can be explained by the fluorescence phenomenon due to the organic character of copper phthalocyanine [20]. The existence of copper phthalocyanine in these glazes suggest that the roofing tiles were undergone restorations in the past [21].



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Figure 5: Raman spectra of green glaze of MEK-GGRTMBIM sample.

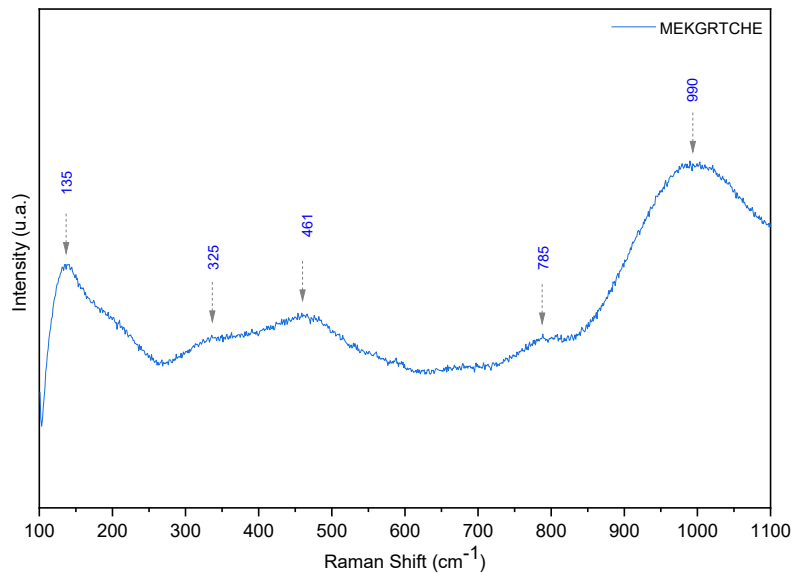


Figure 6: Raman spectrum of glaze of MEK-GGRTGHME sample

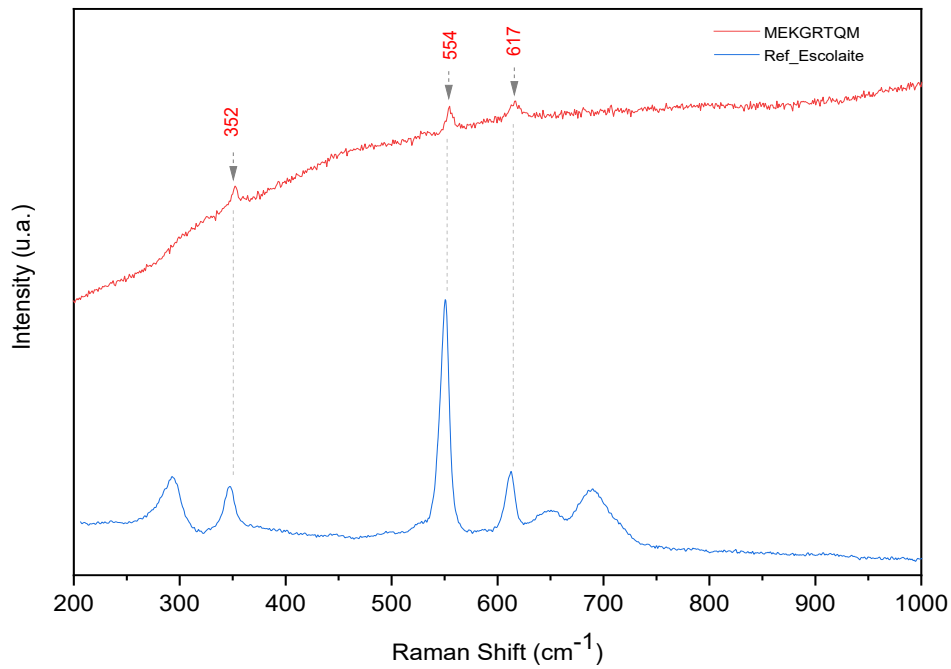


Figure 7: Raman spectra of green glaze of MEK-GGRTQM and reference of Eskolaite

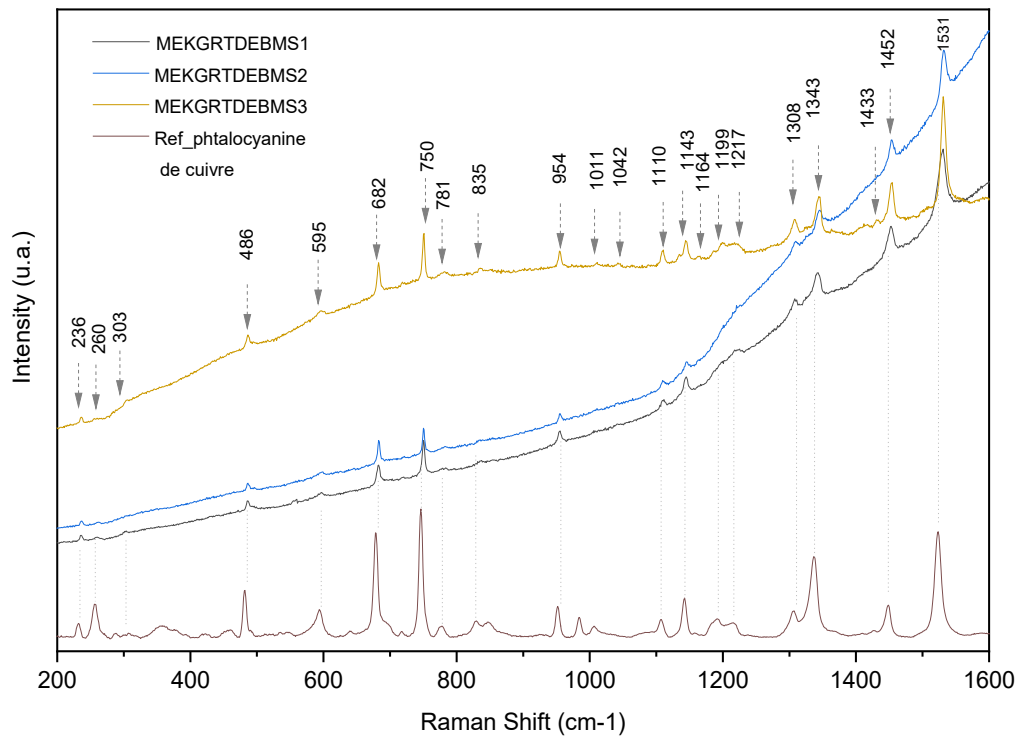


Figure 8: Raman spectra of green glaze of MEK-GGRTDEBM and reference of copper phthalocyanine

3.4 Mineralogical composition of ceramic bodies

The X-ray diffraction patterns recorded on powder of ceramic bodies of MEK-GGRTMBIM, MEK-GGRTDBM, MEK-GGRTQPM and MEK-GGRTGHME samples are shown in figures 9 to 12. They highlight quartz as the most abundant crystalline phase. Anorthite, (CaAl₂Si₂O₈) gehlenite (2CaO·Al₂O₃·2SiO₂ and diopside (MgCaSi₂O₆), so-called high temperature phases, are

also identified. The presence of the newly formed minerals (Anorthite, gehlenite and diopside) in the ceramic bodies of samples let know that calcic clays have been used and their firing temperatures were around 950°C [6; 7; 22; 23]. Calcite and hematite have been detected but in low amount. The presence of hematite indicates that the firing of the tiles was carried out in an oxidizing atmosphere during production [6; 9; 13; 24; 25]. The XRD pattern of the ceramic body of sample MEK-GGRTGHME presents the wollastonite phase in addition in comparison to other samples studied. Amount of calcite is low, because of it contributes to the neo-formed phases (Anorthite, gehlenite and diopside).

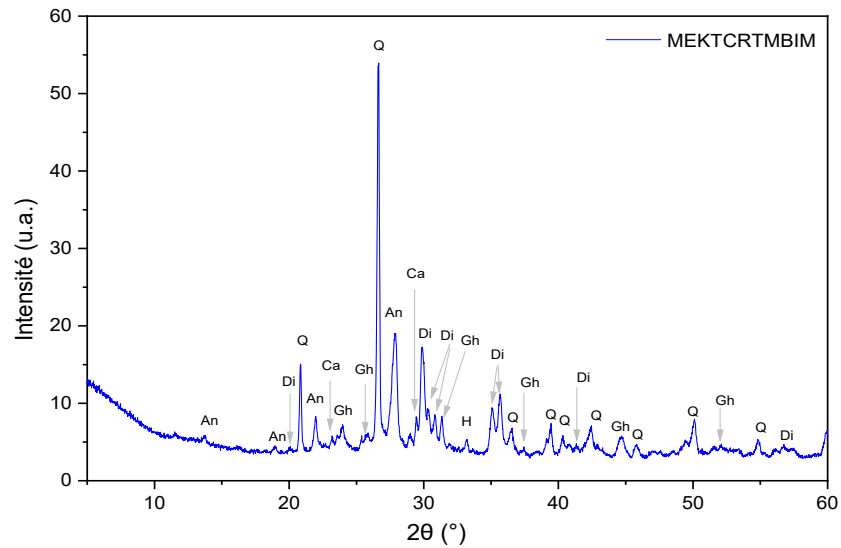


Figure 9: XRD pattern of ceramic body of sample MEK-GGRTMBIM.
[Quartz (Q) ; Gehlenite (Gh) ; Anorthite (An) ; Diopside (Di) ; Calcite (Ca); Hematie (H)]

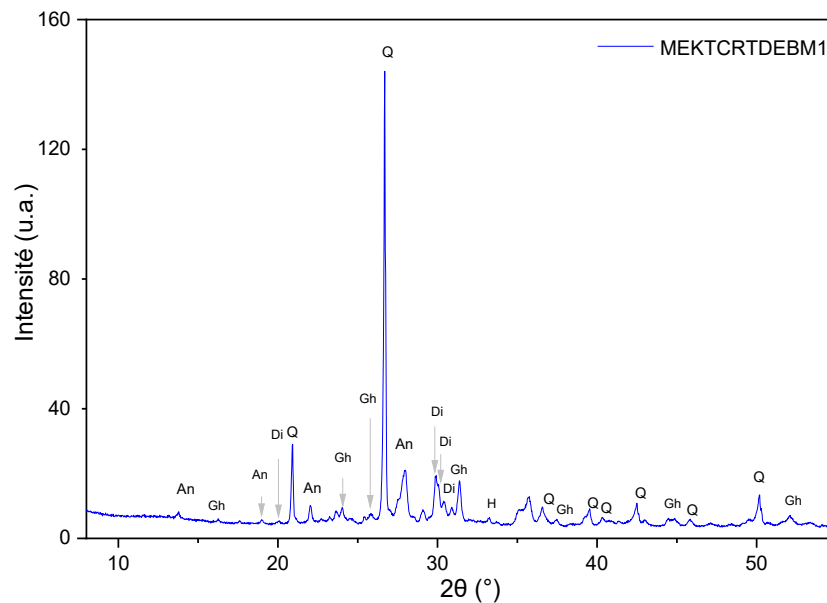


Figure 10: XRD pattern of ceramic body of sample MEK-GGRTDBM
[Quartz (Q); Gehlenite (Gh) ; Anorthite (An) ; Diopside (Di) ; Calcite (Ca); Hematie (H)]

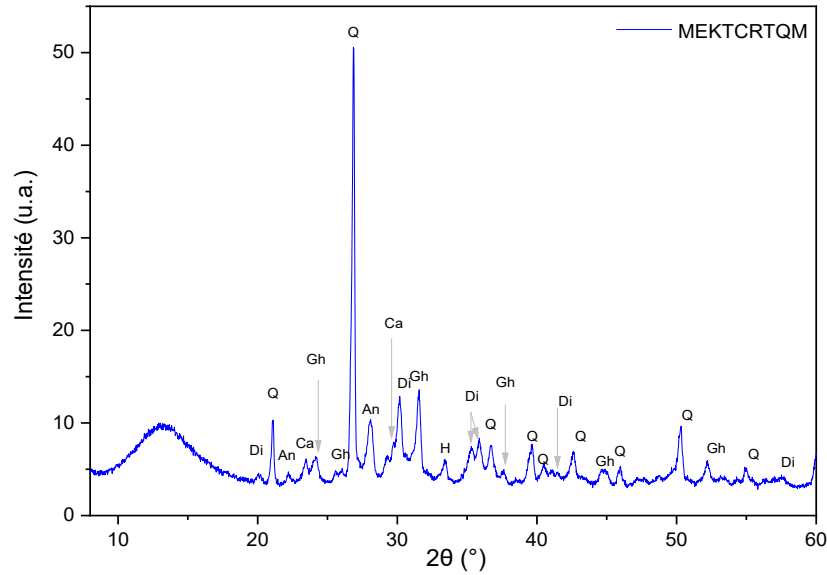


Figure 11: XRD pattern of ceramic body of MEK-GGRTQPM sample [Quartz (Q) ; Gehlenite (Gh) ; Anorthite (An) ; Diopside (Di) ; Calcite (Ca); Hematie (H)]

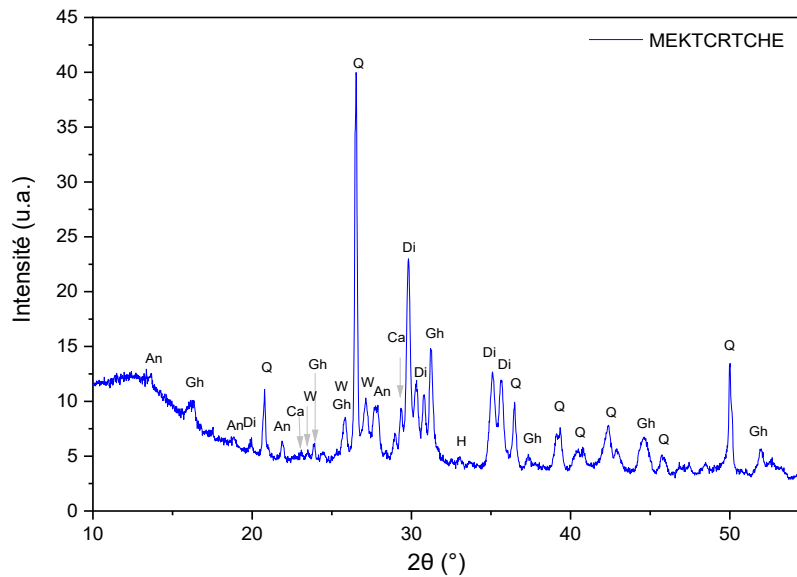


Figure 12: XRD pattern of ceramic body of MEK-GGRTGHME sample [Quartz (Q) ; Gehlenite (Gh) ; Anorthite (An) ; Diopside (Di) ; Calcite (Ca); Hematie (H); wollastonite(W)]]

Conclusion

In this work, we have characterized the green glazes of Moroccan glazed roofing tiles. We have obtained access to some technological parameters such as, chromophore elements, coloring phases, firing temperature and conditions of firing, involved in the manufacture of glazed roofing tiles coming from the four sites.

Chromametry has shown difference in chromatic coordinates (L, a*, b*) of green glazes. Optical reflectance spectroscopy has shown that the green colour of glazes is mainly related to the properties of light absorption by metal ions:

- Trivalent chromium ions Cr^{3+} for green glazes of the roofing tiles of Dar El-Beida Palace and Quara Prison in Meknes
- Copper ions Cu^{2+} for green glazes of samples coming from Medersa Bou Inania in Meknes and graveyard of Hibous Mdaghra in Errachidia.

Raman microspectroscopy has identified the colouring phases, namely escholaite ($\alpha\text{-Cr}_2\text{O}_3$) for glaze from Quara prison, copper phthalocyanine mixed with a chromium-based pigment for Dar El-Beida Palace. For glazed tiles from Madrasa Bou Inania (Meknes) and Hibous Mdaghra (Errachidia), the green color is due to dissolution of copper in a vitreous matrix in lead glazes opacified with tin oxide and/or Naples yellow. Ca-rich clays fired at about 950°C in an oxidizing atmosphere have used to make ceramic bodies composed mainly quartz. Other phases as anorthite, gehlenite, diopside, hematite and calcite have been also detected. The comparative study has highlighted difference in manufacturing technology between green glazes of glazed roofing tiles coming from the four sites.

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