



Investigation of inks, pigments and paper in four Moroccan illuminated manuscripts dated to the eighteenth century

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Abstract The heritage left by the Arab world in the history of science is directly related to the innovations in both the manufacturing of paper and the production of ink. Four Moroccan manuscripts dating to the eighteenth century, conserved at the royal library of Rabat, have been analyzed by X-ray diffraction (XRD), energy-dispersive X-ray fluorescence spectrometry (EDXRF), scanning electron microscopy coupled to energy dispersive X-ray spectroscopy (SEM–EDS), Raman and attenuated total reflection Fourier transformed infrared spectroscopy (FTIR-ATR). The combination of the Raman, EDS, and EDXRF spectroscopies results allows us to Characterized the inorganic inks, pigments and fillers used in paper making process. Iron-based ink was used for writing the text for all manuscripts. The main pigments used in the titles and in the illuminated part are found to be vermilion and red ochre in red samples, azurite with barium white and ultramarine in blue color, lead chromate in yellow color, copper and arsenic based ink in green color, carbon black for black color and gold. The main fillers identified in paper are calcite and kaolin. FTIR-ATR and Raman analysis revealed the presence of the characteristic bands of cellulose, the main component of paper. XRD confirms the presence of the fillers detected by FTIR-ATR. Finally, SEM allows to have a better knowledge of the typical morphology of the paper highlighting some effects of the degradation process.

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1 Introduction

Illuminated manuscripts are among the most precious artworks, as the palettes of the colorants used by ancient illuminators and scribes included many different colorants [1].

Chemical analysis of inks and paints is mostly restricted to coloring agents' identification [2]. Coloring agents' identification in manuscripts can provide valuable information for conservators, restorers, curators' museum, and art historians [3, 4].

For art historians, it is important to have knowledge of the nature of the colorants used on manuscripts, to understand the ancient techniques, to attribute the manuscript to a particular artist or workshop, to authenticate and to date the manuscript [5]. However, for restorers, coloring materials characterization can help to distinguish the original colorant from restored or portions added later. Analyzing coloring materials is crucial before applying any chemical or other treatment. It can help the restorers to take important decisions such as those regarding the removal of external layers, or the choice of the matching color for the retouches [6]. Finally, for conservators, depending on their nature, some colorants may be sensitive to light, humidity, gaseous atmospheric pollutants, or heat, which may require specific storage [1].

Many analytical techniques have been used for pigments identification, including energy-dispersive X-ray fluorescence spectrometry (EDXRF), X-ray diffraction (XRD), micro-Raman spectroscopy, Fourier-transformed infrared (FTIR) spectroscopy and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), which are some of the most suitable ones for this purpose [7, 8]. The coupling of elemental and molecular characterization methods can overcome the limitations of individual techniques and increase information gained from analysis [9].

Energy-dispersive micro-X-ray fluorescence spectroscopy (μ -EDXRF) allows collecting the elemental and spatially resolved information on major and minor constituents of colorants in a non-destructive way [10].

However, micro-Raman spectroscopy allowed rapid and unambiguous *in situ* identification of most pigments applied by the calligraphers/scribes without damaging the valuable manuscripts [8, 11, 12]. It is a vibrational technique based on the fact that a small part of incident radiation is scattered in elastically by a material [13].

Tanevska et al. [14] have been using micro-Raman spectroscopy to investigate the chemical nature of pigments and inks present in five Islamic illuminated manuscripts, dated from 16th to 18th century. Burgio et al. [15] identified the presence of vermilion, iron oxide, azurite, malachite, white lead and lead tin yellow type I on three illuminated German manuscripts by means of Raman microscopy.

SEM-EDS have been used recently in ancient documents to perform elemental micro-analysis [16]. Energy-Dispersive Spectrometry (EDS) allows to determine the elemental composition of ink and pigment present in manuscripts by means of coupling with scanning electron microscopy (SEM) [17]. Furthermore, the observations carried out by SEM magnify the typical paper morphology, highlighting the effects of weathering on the cellulose matrix [18].

FTIR spectroscopy may represent a useful analytical method to determine the supporting material, binders, inks, and pigments in historical documents [19, 20]. Many studies [21–23] demonstrated that IR spectroscopy is an indispensable tool for the characterization of inks and pigments in ancient manuscripts. The FTIR spectroscopy was used to characterize the blue pigments in different polychrome works of art [24].

Besides more frequent spectroscopic methods (EDXRF, Raman, SEM-EDS, FTIR), XRD represents a very effective tool for indisputable determination of practically all inorganic crystalline pigments and materials [25–27]. Micro-X ray diffraction (μ -XRD) is a suitable



Fig. 1 Manuscripts under study dating to the eighteenth century belonging to the Royal library of Rabat and details of the analyzed ink, illumination, and paper areas of each manuscript

Table 1 Description of the analyzed manuscripts

Manuscripts	Format (mm)	Ink colors
P1	155 × 187	Black, gold, light brown and brown
P2	145 × 185	Black, purple and green
P3	158 × 197	Black and blue
P4	160 × 218	Black

technique for the identification of mineral components in colored layers of paintings, especially when substances with similar or even identical chemical composition exist in a range of structural polymorphs, e.g., aluminosilicates in earthy pigments or copper-based pigments [19]. XRD can provide information about the crystallinity degree of cellulose, related to its degradation level, and can confirm the nature of fillers detected therein [28].

The aim of this research is to give a fundamental knowledge on the history of the use of inks, pigments and supporting materials (paper) commonly and mostly used on Moroccan illuminated Islamic Manuscripts related to a specific period (18th century). Four Moroccan manuscripts dating the 18th century conserved at the royal library of Rabat have been analyzed by EDXRF, SEM-EDS, Raman and FTIR-ATR spectroscopies and XRD, in order to determine the molecular and elemental composition of the supporting material and different types of inks and pigments used by the calligraphers/scribes.

2 Materials and methods

2.1 Description of the manuscripts

Four manuscripts (P1, P2, P3 and P4) (Fig. 1), dated to the 18th century and belonging to the Royal library of Rabat, have been analyzed. All the manuscripts are made of paper and they have different format (Table 1). A combination of a variety of colors was used by the scribes for writing the four manuscripts (Table 1). Black ink was used for the main text and the colored inks were used for rubrics, titles, and to mark important words for P1, P2 and P3. However, the manuscript P4 was scribed only by black ink. The text of P1 is surrounded by golden lines.

The manuscripts are in good condition, with the exception of P4 that presents some traces of photo-degradation, which may be due to the additives used in the production of the manuscript (inks, sizing, fillers, etc.) and/or to the storage conditions [32].

Manuscript P1 was decorated with a beautiful illumination and miniature; the illumination part presents the title of the manuscript written in gold in Arabic character. P1 has been illuminated with various geometric forms and flowers in different colors. The color palette is strong and bright, and the illumination is in a very good condition, despite some abrasion of the green and red areas.

2.2 Characterization techniques

The supporting materials of all manuscripts and every colored area have been analyzed. The measurements with EDXRF and Raman spectroscopy were performed directly on the documents, while the analysis by XRD, FTIR-ATR and SEM-EDS was carried out on micro-samples.

2.2.1 Raman spectroscopy

Raman spectra were obtained directly on the manuscripts by using a using an XploRA confocal spectrometer from Horiba-Jobin Yvon GmbH (France) equipped with an air-cooled iDus CCD detector. Spectra were obtained using a 785 nm laser wavelength, a 100× magnification objective, a 300 μm pinhole, a 200 μm entrance slit, and a 1200 lines/mm diffraction grating. The spectral resolution is 4 cm⁻¹. Spectra deconvolution was performed using LabSpec (V5.78) software. The spectrometer was calibrated with the silicon Raman band at 520.7 cm⁻¹. Spectra were identified with the Horiba Spectral ID database and by using reference spectra in the literature.

2.2.2 X-ray diffraction (XRD)

XRD experiments were performed on an X-Ray diffractometer (X'Pert Pro model, Panalytical, London, United Kingdom) operating with Cu Kα radiation ($\lambda=1.5406 \text{ \AA}$). The current was adjusted to 30 mA and the voltage was increased to 40 kV. The reflection angle 2θ is in a range between 10° and 70°, it changes of 0.016° with a step of 40 s.

2.2.3 Attenuated total reflectance Fourier transform infrared spectroscopy (FTIR-ATR)

Spectra were obtained in the attenuated total reflection mode using an infrared spectrometer (Bruker Vertex 70 model, Germany) equipped with a sampling accessory diamond crystal. The analyses were carried out at room temperature and ambient humidity. All the spectra were acquired between 4000 and 400 cm⁻¹ with a spectral resolution of 4 cm⁻¹ and 16 scans in order to exploit the instrumental built-up noise reduction algorithm. The spectra were collected in attenuated total reflection mode.

ATR was applied in micro-sample and directly on the paper (recto) without any kind of preparation. One folio for each sample was analyzed. Three points per folio were studied. The spectra collected in the three points for each folio are the same.

2.2.4 Triaxial geometry energy-dispersive X-ray spectrometry (EDXRF)

The paper supports were analyzed directly using a spectrometer with orthogonal triaxial geometry between the side window X-ray tube (W, 100 kV, 80 mA max.), (PHILIPS PW 2184/00, the Netherlands), the secondary target (Mo), the sample and the detector. A nitrogen cooled Si(Li) detector (Oxford, UK) with a 30 mm² sensitive area, 8 μm beryllium window and 135 eV energy resolution for 5.9 keV was used. This geometry significantly reduces the background of the measured spectra by eliminating the *Bremsstrahlung* produced in the X-ray tube through crossed polarization in the secondary target and in the sample. In this way, a better peak-to-background ratio is obtained, improving the detection limits and leading to higher sensitivity, when comparing with other EDXRF setup geometries. The X-ray generator was operated at 50 kV and 20 mA for 1000 s. The spot size was measured with a radiographic film producing an ellipsoid image with 20 mm × 15 mm. The quantitative evaluation of the paper support was made for detected elements above silicon using the X-ray Fluorescence Automatic Evaluation System (XRFAES), which is based on the fundamental parameters method [29]. The accuracy of the method was validated by comparing the elemental content of reference standards with known elemental concentrations: orchard leaves, NBS standard reference material 1571, the matrix of which is cellulose. These were in good agreement with the calculated concentrations [30]. Ten measurements were acquired at the paper support of each manuscript under study.

2.2.5 Energy-dispersive micro-X-ray fluorescence spectrometry (μ-EDXRF)

For inks and pigments characterization, manuscripts were directly analyzed using the commercial M4 Tornado μ-EDXRF spectrometer (Bruker, Germany). The spectrometer is equipped with a side window X-ray tube (Rh, 50 kV, 600 μA) with a polycapillary lens that accounts for a spot size down to 25 μm for Mo-Kα at the sample; an energy-dispersive Silicon-Drift-Detector with 30 mm² sensitive area and energy resolution of 142 eV for Mn-Kα. The X-ray generator was operated at 50 kV and 300 μA. Analyses were carried out under 20 mbar vacuum conditions. Spectra acquisition and evaluation were carried out using Esprit software from Bruker.

2.2.6 Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS)

Environmental scanning electron microscopy scans were recorded by means of a Quanta 200 MK2 (FEI, the Netherlands) associated with an EDS microprobe. This microscope is a high-resolution imaging equipment that does not require any sample coating or preparation. SEM images have been obtained using the secondary electron detector at different magnifications. Observations were carried out directly on the paper samples without any kind of sample preparation. SEM measurements were made at 5 to 20 kV accelerating voltage in a pressure of 130 Pa. An energy dispersive X-ray microanalysis system allowed us to obtain elemental analysis.

3 Results and discussion

In the following, the experimental results are discussed in three sections, one concerning the characterization of the cellulosic support, the other concerning the identification of inks and the last one concerning the identification of pigments used in the illuminations.

3.1 Paper characterization

Firstly, we proceed to a characterization of the paper supports of all samples, and then the expertise of the coloring materials is presented and discussed color by color.

The FTIR-ATR spectra of the cellulosic support of the four manuscripts P1, P2, P3 and P4 are given in Fig. 2a. By examining the spectra of the individual samples (P1, P2, P3 and P4), we can observe the presence of a broad peak in the range $3700\text{--}3000\text{ cm}^{-1}$, centered at 3434 cm^{-1} for P1 and P3, at 3445 cm^{-1} for P2 and at 3423 cm^{-1} for P4 (Fig. 2b). This band is related to the stretching vibration of alcohol hydroxyl bonded groups O–H [31–33].

The characteristic stretching vibration bands of CH are identified at 2923 cm^{-1} for ν_s (CH_2), ν_{as} (CH_2) at 2858 cm^{-1} and $\delta\text{ CH}_2$ between $1453\text{--}1459\text{ cm}^{-1}$ (Fig. 2b) [34].

It should be noted that the bands presented in the spectra at $1640\text{--}1644\text{ cm}^{-1}$ (Fig. 2c) is related to the adsorbed water for all samples [35].

Figure 2c represents the $1700\text{--}500\text{ cm}^{-1}$ region assigned to different stretching vibrations of various groups of cellulose (fingerprint region) [36]. We observe the absorption band at 1118 cm^{-1} for P3 and P4 and at 1124 cm^{-1} for P2 which is attributed to the ν (C–O–C) stretching vibration of the $\beta(1\text{--}4)\text{-glucosidic}$ linkage [37]. However this band is absent in P1. The band at 1453 cm^{-1} originated from the CH_2 symmetric bending at C6 [38] which also overlaps with the characteristic band of calcium carbonate (corresponding to the asymmetric C–O stretching mode in CO_3^{2-} groups). The absorbance at 1384 cm^{-1} in all samples arises from the in-plane C–H bending vibrations [39]. According to Hajji et al. [31] the band located at 1050 cm^{-1} corresponds to the stretching (ν (C–O)) of secondary alcohol detected only in

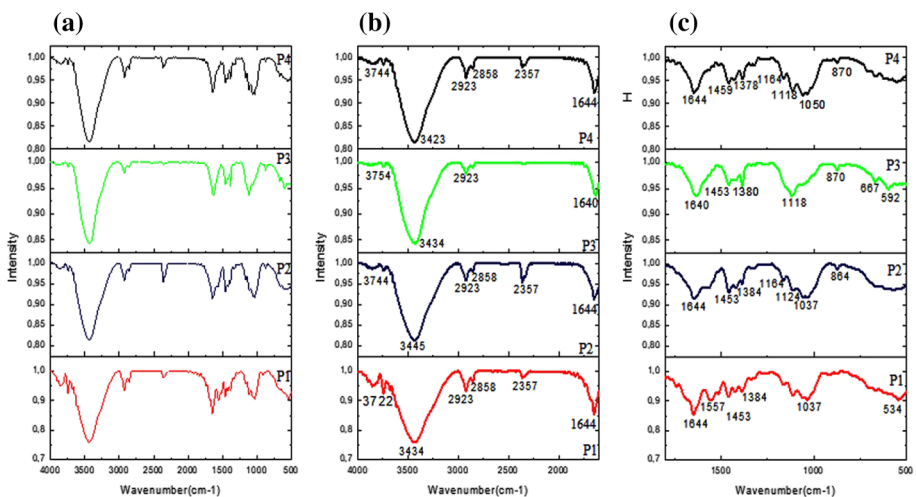


Fig. 2 FTIR -ATR spectra of cellulose support of P1, P 2, P3 and P4 recorded in different range: **a** $4000\text{--}500\text{ cm}^{-1}$, **b** $4000\text{--}1600\text{ cm}^{-1}$ and **c** $1700\text{--}500\text{ cm}^{-1}$

Table 2 Main bands and their assignments according to the literature

Band position (cm ⁻¹)	Band assignments	References
3423–3445	$\nu(\text{OH})$: valence vibration of hydrogen bonded OH groups	[31–33]
3000–2800	$\nu(\text{CH})$ groups	[34]
1644	δ of adsorbed water	[40]
1557	δ (N–H) and ν (C–N) of amide II	[31, 40]
1453	ν_{as} (C–O) in CO_3^{2-} groups of CaCO_3 and $\delta(\text{CH}_2)$ at C6 of cellulose	[41]
1384	in-plane δ (CH) groups	[39]
1118–1124	(C–O–C) at β -glucosidic linkage (crystallized cellulose I)	[37]
1037	ν (C–O)	[31]
870	ν_{s} (C–O) of CaCO_3	[33]
592	δ (Si–O) in kaolin	[42]

ν stretching; δ bending; a, asymmetric and s, symmetric

P4, nevertheless in P1 and P2 we have detected another band at 1037 cm⁻¹ which could be attributed to ν (C–O) stretching vibrations of primary alcohol.

The two broad bands at 1644 and 1557 cm⁻¹ that, respectively, assigned to amide I and amide II (due to in plane N–H and C–N stretching vibration) [31, 40] may be related to the presence of sizing materials. The band at 1644 cm⁻¹ is overlapped with that of adsorbed water.

Regarding the sizing materials, the presence of calcium carbonate (Fig. 2c) in the samples P2, P3 and P4 is suggested by the two bands located at 1453 cm⁻¹ (overlapped with δ CH₂) and at 870 cm⁻¹. These absorptions are, respectively, assigned to the asymmetric and symmetric C–O stretching mode in CO_3^{2-} groups [40]. Our results are in accordance with Burgio and Clark [41].

Using FTIR–ATR spectroscopy, we can also suspect the presence of another filler; the kaolin (Al₂Si₂O₅OH₂). Indeed, it should be noticed the presence of two bands located at 3722 cm⁻¹ and 534 cm⁻¹ for sample P1. For sample P3, they are located at 3754 cm⁻¹ and at 592 cm⁻¹ (Fig. 2b, c). These bands are related, respectively, to the silanol group Si–OH and to the angular deformation of the Si–O–Al [42]. The use of these fillers (kaolin and calcite) in the paper making process is confirmed by the XRD, SEM–EDS and EDXRF results. The most important characteristic bands of paper and fillers are summarized in Table 2.

Spectra were identified by using FTIR–ATR reference spectra in the literature [31–42].

The Raman spectra of manuscript P2 supporting material (Fig. 3) revealed the presence of the characteristic bands of cellulose, which involves mainly C–C stretching, C–O–H and C–C–H deformation vibrations. In particular, the band at 1120 cm⁻¹, which is assigned to the symmetric stretching mode ($\nu(\text{C–O–C})$) of the $\beta(1,4)$ -glycosidic linkage [43]. The band at 1379 cm⁻¹ is assigned to C–O–H and H–C–C bending vibrations [44], while the bands at 520 and 379 cm⁻¹ are due to $\delta(\text{COC})/\delta(\text{CCC})$ bending [45, 46].

Figure 4 presents the mean elemental concentration ($\mu\text{g}\cdot\text{g}^{-1}$) of the analyzed papers (P1, P2, P3 and P4). The highest concentrations were observed for Ca, K, Cl and S. Iron is a minor element. A similarity to the S content is observed in manuscripts P1, P2, P3. However, the concentration of Ca in P2 and P4 is higher in P3 and P1, concerning the concentration of K it reaches the highest value in sample P2. The presence of Ca was not surprising since this element is the mean component of the calcite, the common filler used in paper making

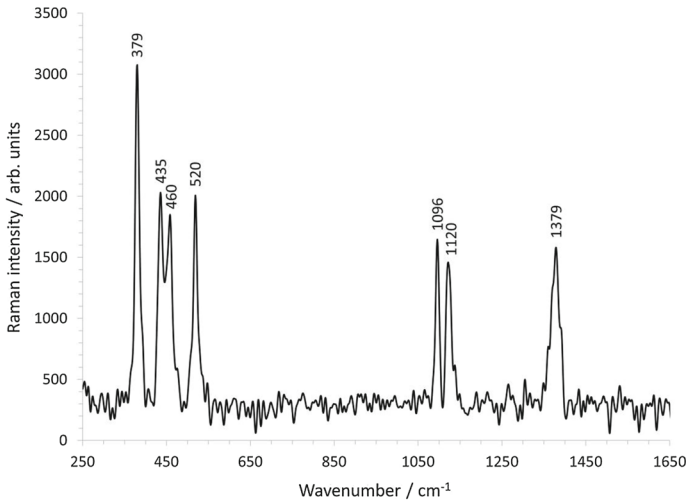


Fig. 3 Raman spectrum of cellulosic support of P2

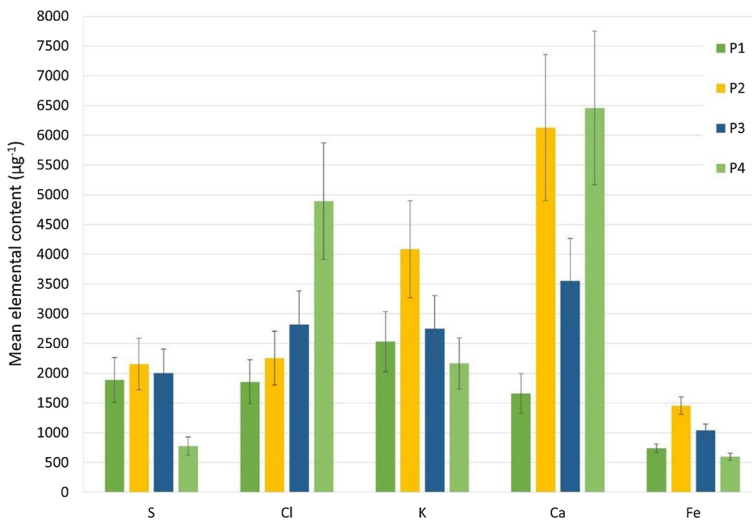


Fig. 4 Comparison of the mean elemental content of the cellulosic support of P1, P2, P3 and P4 obtained by triaxial geometry EDXRF spectrometry

[31, 36]. In addition to calcium, triaxial geometry EDXRF spectrometry results revealed the presence of chlorine that could be related to the water used for the preparation of the supports [26]. The presence of elements sulfur and potassium could indicate the use of alum that reduced the ink absorbency in writing papers. When sized only with gelatin, papers remained readily moisture absorbent [29].

The detection of a small amount of iron in all samples may be presumably due to some iron gall ink residual traces which have been incorporated between fibers, or to the water supply as well as the papermaking process [47, 48].

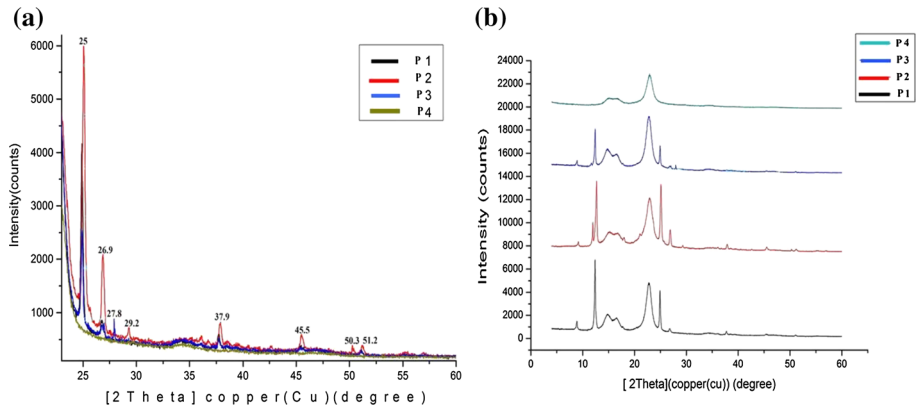


Fig. 5 X-ray diffractometry profiles of papers from P1, P2, P3 and P4

The XRD results of manuscripts P1, P2, P3 and P4 are given in Fig. 5a, b. The X-ray diffractograms of all paper samples show the same diffraction features of cellulose as the dominant phase (Fig. 5a). Cellulose is identified by the characteristic peaks of crystalline fraction at 2θ between 22 and 23° and that correlated to the amorphous fraction at 2θ between 15 and 16° [39]. The peak observed at $2\theta=25^\circ$ in P1, P2 and P3 correspond to the barium sulfate, but according to the literature [49], barium sulfate is introduced in the 19th century as paper filler and our manuscripts are dated the 18th century. According to a research done by specialized historians of the royal library, the manuscripts are dating to the 18th century. However, the presence of barium sulfate confirmed by XRD may suggest that these manuscripts are produced in the 19th century, because the use of this filler was not applied before.

The X-ray diffractogram (Fig. 5a, b) of P1, P2 and P3 showed, not only the characteristics peaks of cellulose, but also the peaks corresponding to the fillers used in the papermaking process (kaolin at $2\theta = 12.63$ and 26.9°). The use of calcite confirmed by the presence of the peaks located at $2\theta = 29.31$, 36.9 , 45.5 , 50.3 and 51.2° for P2, and at $2\theta = 27.8$, 36.9 , 45.5 , 50.3 and 51.2° for P3 [50]. Concerning P4, XRD results revealed only the presence of cellulose as the dominant phase and no filler had been detected. However the FTIR-ATR analysis elucidates the presence of calcite in this sample.

Based on the literature [26], the presence of talc [$Mg_3Si_4O_{10}(OH)_2$] is confirmed by the peaks located at $2\theta = 10^\circ$, $18-20^\circ$, and 28° . In Figure 5, the presence of a shoulder at $2\theta = 8, 8^\circ$ for P1 and P3 and another one at $2\theta = 9.13^\circ$ for P2 may be linked to the presence of talc, but the absence of the peaks at $2\theta = 18-20^\circ$ and 28° would exclude the use of this filler. It is certainly due to some impurities or contaminants. Furthermore, SEM-EDS did not reveal the presence of Mg.

The observation performed by scanning electron microscopy (SEM) helped us gain better knowledge of the typical morphology of the different analyzed paper manuscripts. Figure 6 presents the SEM micrographs of the cellulosic support of P2 and P3 (the images of P1 and P4 are not presented in the figure). The distribution of the fibrous structure is heterogeneous, and their orientation is random. Some breakage is observed in the two samples as illustrated in Fig. 6. It should be highlighted that some dust and white spots are spreading over the entire surface of the paper, which could correspond to the fillers used in paper making process [48–51].

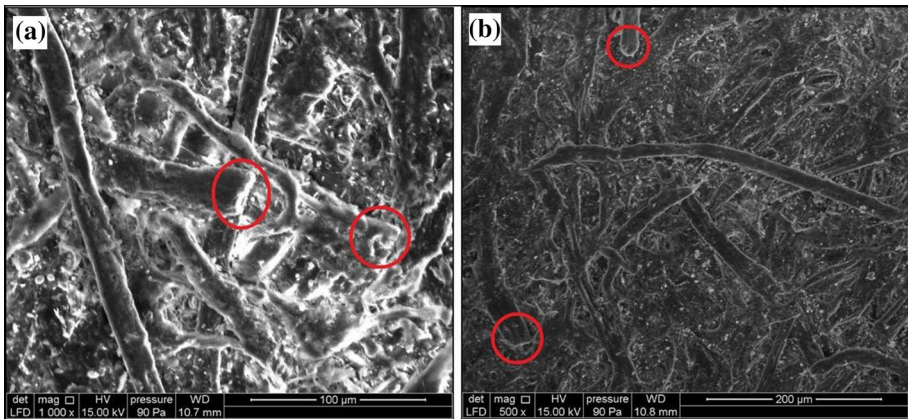


Fig. 6 SEM micrographs of the cellulosic support of the manuscript **a** P2 and **b** P3

3.2 Inks and pigments

The manuscripts P1, P2, P3 and P4 have been scribed by a combination of different ink colors as described in Table 1.

The manuscript P1 presents an illumination and a miniature illustration characteristic of the 18th century, where mixtures of coloring materials were employed to obtain a distinct hue.

All the colored and inked areas of all manuscripts were analyzed by μ -EDXRF, Raman, XRD, SEM-EDS and ATR-FTIR spectroscopy. It should be noted that the XRD and ATR-FTIR results did not reveal the presence of any compound corresponding to the chemical composition of inks or pigments and Raman analysis only succeeded in pigments identification.

In the following, we first proceed to the characterization of inks present in all samples and then to the identification of the coloring agents used to illustrate the decoration in the manuscript P1.

3.2.1 Characterization of inks

Black ink The main element detected by μ -EDXRF for black ink in all samples corresponds to iron (Fig. 7a). This indicates the use of iron-based ink for the studied manuscripts [26]. The presence of potassium in all manuscripts could come from the contamination of water used in ink making (or from wine, beer, or vinegar sometimes used instead of water to prevent the ink from freezing in winter) [26, 51–55, 57]. The presence of Ca emission line in all black inks may originate from the underlying paper support.

Brown ink The μ -EDXRF spectrum obtained in brown ink (Fig. 7b) for the P1 showed the presence of iron which, could indicate the use of iron-based ink [57, 66]. According to Hahn et al. [58], the brown ink contains a complex mixture of several decomposition products such as purpurogalline or ellagic acid (generally in combination with different iron oxihydrates). From that, we may suggest that this ink is mixed with iron oxihydrates.

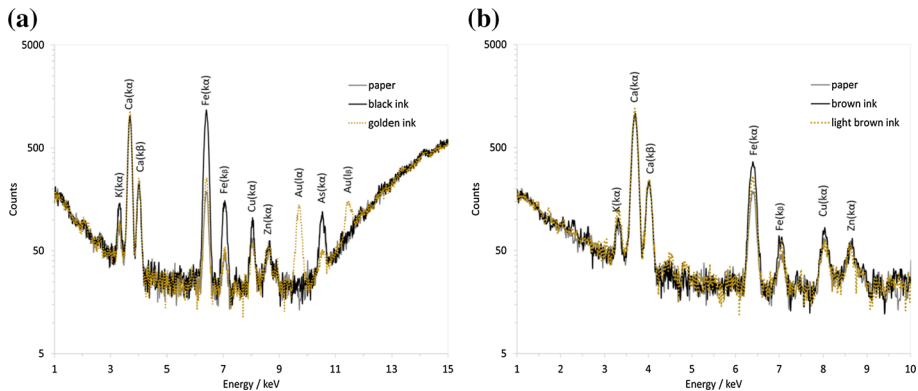


Fig. 7 μ -EDXRF spectra obtained at P1 of **a** paper support, black and golden inks **b** paper support, brown ink and light brown ink

Light brown ink No differences were identified between μ -EDXRF spectra from light brown ink and of the cellulosic support, except the presence of iron in very small amount. This could suggest that it is an iron based in very low concentration [26].

Gold ink Gold was used for writing the titles, important sentences in P1. The high intensity of Au line detected by μ -EDXRF confirms the use of gold (Fig. 7a).

Purple ink Aceto et al. [16] reports that no inorganic elements of purple pigment were available. Purple color was produced by using dyes or a mixture of red and blue pigment. The EDXRF spectrum obtained in purple area reveals no other elements than the ones present in the support. From that we suppose the use of organic dye.

Green ink The EDXRF analysis in green area (Fig. 8) revealed the presence of a high amount of Cu and As. The presence of these elements could be ascribed to the use of green copper arsenate (Scheele's green copper (II) arsenate or emerald green copper (II) ethanoate tri-copper (II) arsenate) [59].

Blue ink Copper distribution obtained by μ -EDXRF of the blue ink present in P3 (Fig. 9) suggests the use of azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$). Barium white (BaSO_4) was probably mixed used with this ink, according to Ba distribution [60, 61]. Furthermore, the detection of Al, Si, and S may also suggest the use of ultramarine ($\text{Al}_6\text{Na}_8\text{O}_24\text{S}_3\text{Si}_6$). According to Picollo et al. [62] and Delaney et al. [61], these results can be interpreted as a thin layer of ultramarine applied on the top of azurite mixed with barium sulfate in selected areas to achieve the deeper blue color. Azurite mixed with barium sulfate, has been detected in our previous study [26].

Table 3 resumes the EDXRF keys elements identified in the analyzed inks.

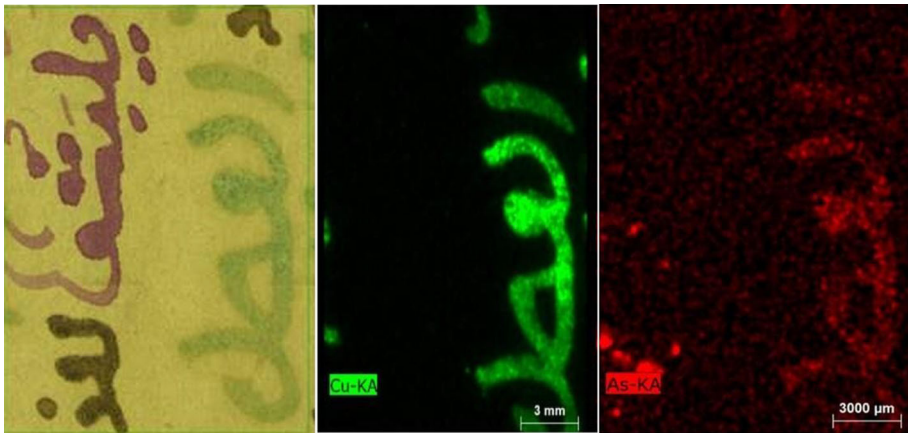


Fig. 8 Copper and arsenic distribution obtained by μ -EDXRF at P2

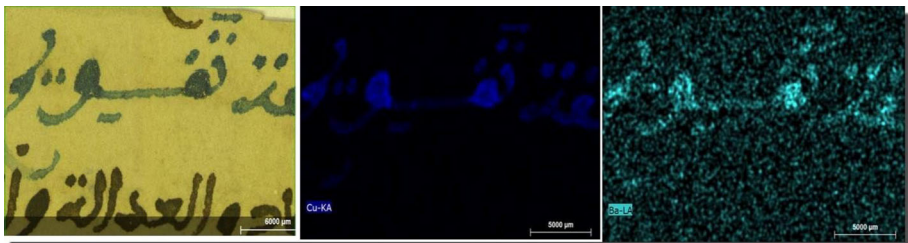


Fig. 9 Barium and copper distribution obtained by μ -EDXRF at P3

Table 3 the Analyzed inks with keys elements of EDXRF

Inks	EDXRF Keys
Black ink	Fe, K, S
Brown ink	Fe
Light brown	Fe
Gold	Au
Blue	Ba, Cu, Al, Si, and S
Green	Cu and As

3.2.2 Characterization of pigments

The manuscript P1 presents an interesting and a nice variety of hues. Figure 10 shows the different colored areas measured on the illumination and miniature of this manuscript.

The illumination of sample P1 Red pigment: Through visual observation of the illuminated part of sample P1 (Fig. 10), we observe a wide area covered in red colors (points 3 and 8).

The Raman spectroscopy (Fig. 11a) indicates the use of vermilion (HgS) by the presence of the characteristic bands of vermilion, located at 253, 285 and 344 cm^{-1} [63]. Furthermore, Pb was also detected in these points as exhibited in the mapping results obtained by μ -EDXRF

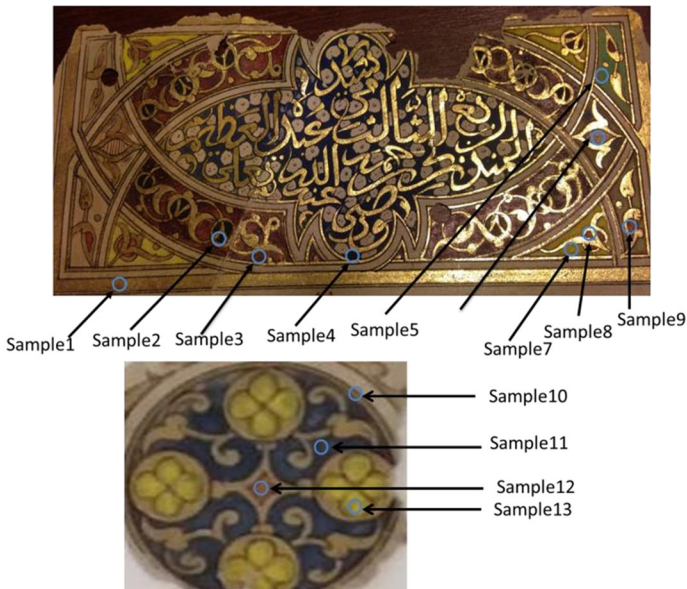


Fig. 10 The illuminated and miniature part of sample P1, indicating the measurement points of the different analyzed pigments (1–13)

in Fig. 11b, which could suggest the use of lead white in the under paint layer or it may be used as a mixture with vermilion [64].

The EDS spectra analysis confirms these results through the very intense Hg and S peaks in the spectra of the measured sample [8].

The natural mercuric sulfide is a very expensive pigment at the time, which was frequently used by artists from antiquity until the 20th century [65].

Iron distribution obtained by μ -EDXRF at another red color area, suggests the use of red ochre Fe_2O_3 (reddish iron earth pigment).

Blue pigment: Raman spectroscopic analysis (Fig. 12) in the blue area, revealed the presence of the characteristic bands of ultramarine blue ($540, 578, 803, 1089 \text{ cm}^{-1}$) [8, 66].

According to the literature [67], natural ultramarine is the most expensive pigment among the palette of blue colors; it was obtained from the mineral lapis lazuli. This valuable pigment was found to be applied in the Islamic manuscripts [68].

Yellow pigment: The Raman spectrum (Fig. 12) collected on yellow area, shows strong bands at 843 and 360 cm^{-1} as well as another weak bands at $336, 372$ and 404 cm^{-1} . According to the literature [69], these bands are characteristic of lead chromate PbCrO_4 . The μ -EDXRF and EDS spectra and the elemental mapping obtained by μ -EDXRF (Fig. 11b) results confirmed the presence of lead chromate by the detection of the lead and chromium. According to the literature, in 1797 Vauquelin reported the discovery of chrome yellow [70] and the recognition of lead chromate as a pigment did not come until 1803 or 1804 [71]. Then this is another reason to suggest that manuscript is dating to the 19th century.

Green pigment: The EDS results and the elemental map obtained by μ -EDXRF (Fig. 11b) of green color, revealed the presence of As associated with Cu which could indicated the use of emerald green ($\text{Cu}[\text{C}_2\text{H}_3\text{O}_2] \cdot 3\text{Cu}[\text{AsO}_2]_2$) or Scheele's green ($\text{Cu}(\text{AsO}_2)_2$) in green area

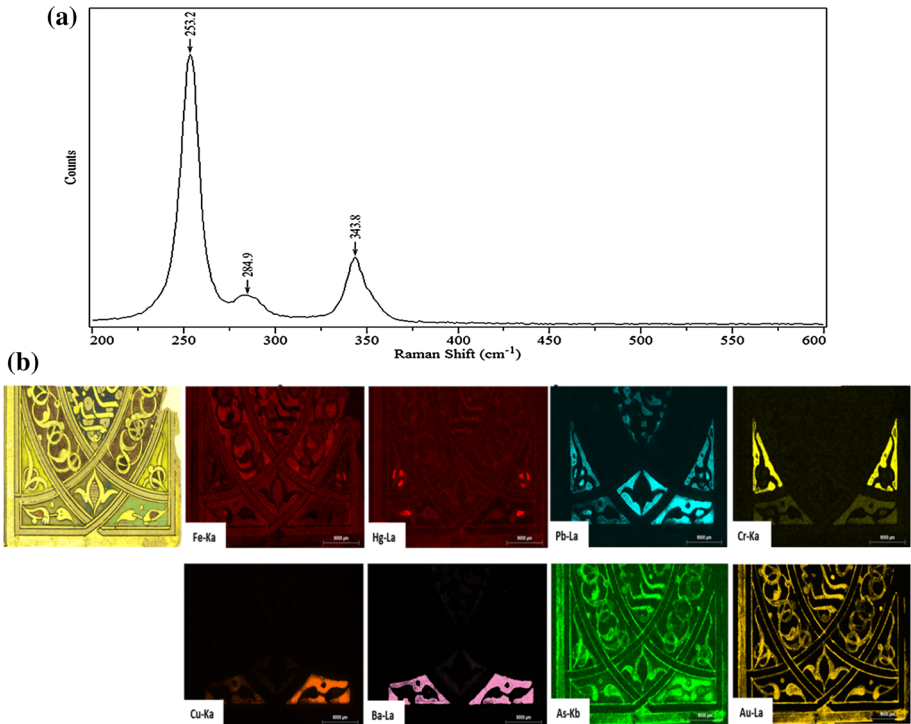


Fig. 11 **a** Raman spectrum from red area and **b** μ -EDXRF elemental distribution obtained for the manuscript P1

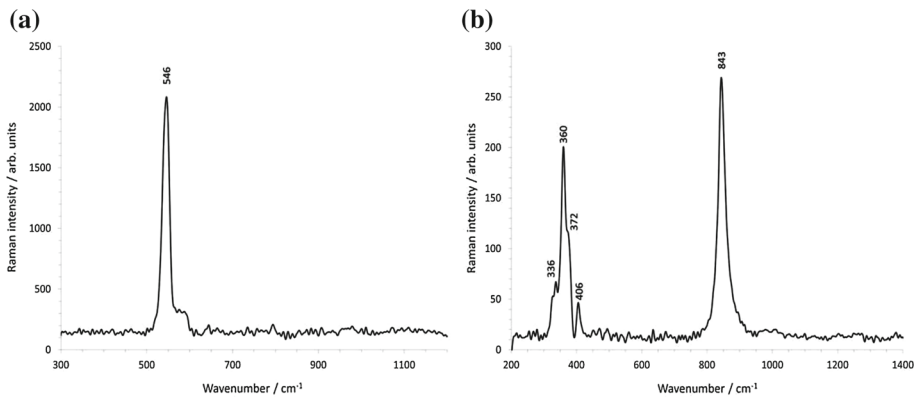


Fig. 12 Raman spectrum corresponding to the analysis of: **a** the blue and **b** the yellow colors in P1

of the illumination part of P1. Our results are in perfect agreement with many studies [59, 72].

Scheele's green was discovered in 1775 and has become very popular as it was one of the best available greens at the time [73, 74]. However, it was recognized to be extremely toxic and the introduction of emerald green in 1814, a pigment with better properties, took Scheele's green out of the artists 'palette [75, 76].

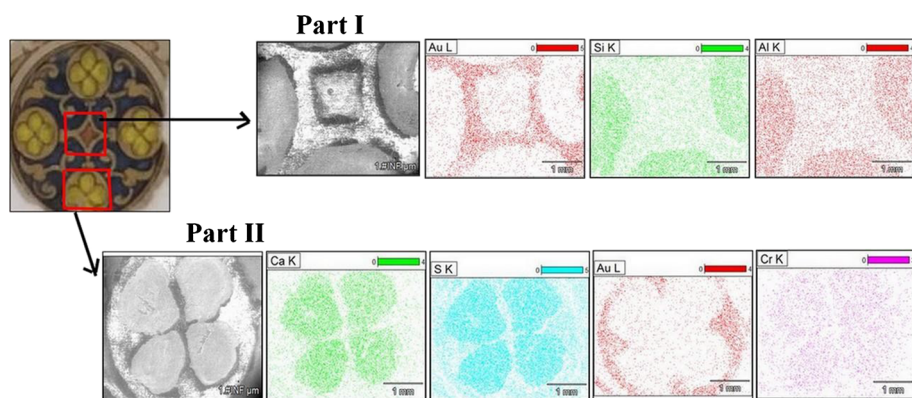


Fig. 13 Distribution of Ca, Au, Si, Al, S and Cr and obtained by EDS mapping at red, yellow, gold and blue pigment from miniature part of manuscript P1

Gold pigment: The EDS results and the elemental mapping (Fig. 11) obtained for the golden region, revealed a high amount of Au indicating its use [75].

Black pigment: The μ -EDXRF spectrum of black area is similar to the one collected from the paper, and no characteristic chemical elements were found in this pigment [77]. It is interesting to note that the intensity of carbon has increased in EDS spectra which affirm the use of carbon black for the black pigments.

Carbon black is the name of a common black pigment, traditionally produced from charring wood. It consists of pure elemental carbon [79]. Raman analysis of the black color clearly shows the presence of carbon-based black pigment, identified by the characteristic bands centered near of 1322 and 1586 cm^{-1} [10].

3.2.3 Miniature part of P1

The miniature part of P1 contains four colors: blue, yellow, red and gold (samples 10, 11, 12 and 13) (Fig. 11). The EDS elemental mapping (Fig. 13) confirms that the colors used for the miniature are similar to those employed in the illumination. Ultramarine $[(\text{Na},\text{Ca})_8[(\text{Al},\text{Si})_{12},\text{O}_{24}]\text{Sn}]$ was used to produce the blue pigment, gold for golden areas and lead chromate PbCrO_4 for yellow pigment.

It should be noted that in the yellow area, other elements were detected (Ca and S), which may probably originate from contamination by the neighboring pigments.

4 Conclusion

This work comprised the use of EDXRF, SEM-EDS, Raman and FTIR-ATR spectroscopy and XRD diffraction for the study of the composition of inks, pigments and paper of four illuminated Moroccan manuscripts dating to the 18th century.

By combining the results obtained by EDXRF, XRD and FTIR, we may conclude that calcite is the main mineral fillers used in the production of the four manuscripts. The use of kaolin is confirmed by XRD in all samples; however, FTIR detects the presence of this filler only in P1 and P3. XRD results detected the presence of barium sulfate in the manuscripts P1, P2 and P3 Concerning P4, XRD results did not reveal the presence of any filler. Based

on the obtained results, with the exception of sample P4, all samples are in good condition of the cellulosic support.

Concerning the characterization of inks and pigments, Raman spectroscopy combined with elemental analysis, such as SEM-EDS and μ -EDXRF enabled characterization of inks and pigments used by the 18th century calligraphers and illuminators of these manuscripts. The obtained results revealed that the palette of inks used in all samples consists of iron based-ink, copper and arsenic based green, copper base blue mixed with barium, gold and an organic dye for the purple color. The palettes of pigments present in manuscripts P1 consists of vermilion, ultramarine, chrome yellow, carbon black and gold.

The age of the manuscript P1, P2, P3 and P4 (18th century) is estimated by the historians of the Royale library (according to their research), so according to our results we suggest that the manuscripts P1, P2 and P3 were produced in 19th century. We have detected barium sulfate as filler in cellulosic support (this filler was applied starting from the 19th century). Another reason to suggest that the manuscript P1 is dating to the 19th century is the detection of lead chromate $PbCrO_4$ (discovered in 1803 or 1804) in yellow areas.

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