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Multi-analytical study of 14th to 19th century illuminated Moroccan manuscripts*

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Abstract. Moroccan manuscripts heritage preserves valuable information regarding different fields of Arabian history and culture. Despite this fact, analytical studies carried out in Moroccan manuscripts are scarce. In this work, we made use of a multi-analytical methodology to study, for the first time, four illuminated manuscripts from the Royal library of Rabat covering the span 14th to 19th centuries. The chemical structure of inks and paper support was identified. Elemental distribution obtained by micro-energy dispersive X-ray fluorescence (μ-EDXRF) showed the use of iron, copper and vermillion in black, blue and red inks, respectively. Arsenic and lead were identified as orange inks in the 17th and 19th century manuscripts, respectively. Quantitative characterization of the paper supports obtained by triaxial geometry EDXRF spectrometry showed high levels of sulphur, chlorine and potassium. Regarding the study of the manuscripts support, cellulose I_β was determined by X-ray diffraction (XRD) in all the analyzed samples. Cellulose fibers observations by scanning electron microscopy showed that the manuscripts are in general, in a good condition. Calcite is the main filler determined by XRD.

Introduction

An illuminated manuscript is a handwritten document adorned with colorful and finely painted miniatures, decorations, letters and borders, added to the text to enrich and underline the contents and the value of the book [1,2]. The choice of the materials used by artists depends on the geographical, cultural and historical context [3]. The identification of these materials (support, ink and pigments) is one of the most important analytical tasks in manuscripts characterization, providing historical, artistic and technological information [4] and is the main issue for obtaining fundamental information necessary in planning an appropriate restoration-conservation procedure [5].

The Moroccan Royal Library of Rabat contains a valuable collection of illuminated manuscripts and other documents on parchment and paper. The importance of this collection relies on the variety of its contents. The library holds more than 20 000 manuscripts in different fields, such as history, Arabic literature, theology, mathematics, astrology, medicine, pharmacy, chemistry and other topics [6]. Despite the historical interest and the high value of this treasure, no scientific investigation was devoted but only some codicological studies. The coloring materials used in these illuminated manuscripts were only described by visual observation [7]. Besides, analytical studies carried out on other Moroccan manuscripts are scarce.

Roger *et al.* [8] studied 21 illuminated manuscripts preserved at the National Library of Rabat corresponding to the period between the 10th and the 16th centuries. They have made use of *in situ* optical and X-ray fluorescence

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spectrometry (XRF) to obtain molecular and elemental information, respectively, concerning the nature of inks and pigments. In all the studied corpus, the manuscripts present a common color range of which red (vermillion, carmine) and blue (lazurite, azurite and indigo) constitute the majority and systematic elements; copper-based green and gold decorate more than 75% of the manuscript, yellow (orpiment, realgar) and orange (*minium*, orpiment with vermillion) participate in the range to a lesser extent. Two other rarer colors are violet and brown. Pure whites (lead white) are generally absent and black (carbon black) is more often used, commonly intended for the outline of the frame, to hem the outside of the trilobed end-of-verse signs or to emphasize the contours of margin vignettes or gilded characters.

Aiming to identify the coloring materials and recipes used by ancient scribes and illustrators in the western Mediterranean region, El Bakkali *et al.* [9] performed an analytical study on 6 Moroccan manuscripts covering different geographic regions, large historical period and produced by different schools. The analyzed inks include black, bright red, pink crimson, blue, dark brown, pale brown-orange and green inks. The non-invasive micro-Raman analysis enabled the identification of iron gall (possibly with copper and saffron), vermillion, azurite, lazurite, realgar/para-realgar, emerald green and orpiment mixed with the indigo mixture. Surface-enhanced Raman scattering (SERS) provided the identification of carmine extract in pink inks. The obtained results lead the authors to believe that the coloring materials and recipes, used by ancient scribes and illuminators over centuries, remained the same in the western Mediterranean region.

Another study by El Bakkali *et al.* [7] confirms the date of production of two Moroccan manuscripts through the identification of three 19th century pigments —synthetic ultramarine blue, Scheele's and emerald green. Other coloring materials identified using a multi-analytical methodology are also reported in this work. Inorganic pigments have been identified and characterized by combining XRF elemental information with molecular infrared and Raman spectrometry investigations. X-ray diffraction (XRD) analyses have been also carried out for the identification of crystalline compounds. Organic dyes have been identified by combining SERS, UV-vis reflection and UV-vis fluorescence spectroscopic techniques.

Dyestuff identification in interleaves from seven 19th-century Moroccan manuscripts —one preserved at the Museum of Islamic Art of Qatar and six preserved at the National Library of Qatar— have been reported by Desvergnes *et al.* [10]. Analyses carried out on micro-samples by high-performance liquid chromatography combined with photodiode array detection (HPLC-DAD), showed that orange interleave papers were dyed with safflower, fuchsia shades obtained with the basic dyestuff Safranine T or with a mixture of mono azo dye-stuff (Ponceau RR, Fast Red AV, Crocein Orange, and Orange II), or even a combination of both.

Aiming to determine the effect of a consolidation treatment on the paper structure of three Moroccan manuscripts with 150, 200 and 800 years, degraded and restored paper samples from these manuscripts have been studied by Hajji *et al.* [11] using infrared spectroscopy (ATR-FTIR), XRD and scanning electron microscopy coupled to energy dispersive X-ray spectrometry (SEM-EDS).

Hajji *et al.*[12] performed a study which consists on an accelerated ageing of fifty samples coming from manuscripts dating from the 16th to the 19th century. Two different ageing procedures were applied; dry heat (at $90 \pm 2\,^{\circ}\mathrm{C}$) and moist heat (100% of relative humidity and $90 \pm 2\,^{\circ}\mathrm{C}$) exposures for 1, 3, 7, 21 and 28 days. A three-analytical approach has been selected to monitor the effects of weathering on paper components by comparing the results of virgin and artificially aged samples. The diagnosis approach was based on the use of ATR-FTIR, XRD and EDXRF.

ATR-FTIR results demonstrated that both dry and moist ageing tests induced cellulose degradation promoted by hydrolysis and/or oxidation. The oxidation of cellulose is the dominant mechanism of alteration during the moist heat process. XRD results showed a remarkable decline in cellulose crystallinity, as evidenced by the strong decrease of the crystalline index (CrI) calculated after accelerated ageing. EDXRF results demonstrated that both accelerated ageing tests affected the paper elemental composition, especially in what concerns Ca amount, although not in all aged papers.

In this study, we present an analytical investigation undertaken for the first time on Moroccan Illuminated manuscripts from the heritage of the Royal library of Rabat. It aims to contribute with knowledge on the origin, manufacturing technology and state of conservation of these historical manuscripts. For this purpose, a multi-analytical methodology covering EDXRF, XRD and scanning electron microscopy (SEM) was applied to the documents to identify the chemical composition of inks and to characterize its cellulosic support. This methodology accounts for raw material and respective degradation products identification and cellulose degradation evaluation through the observation of SEM images and through the determination of its crystallinity index.

Material and methods

Manuscripts description

The manuscripts belong to the Moroccan Royal Library of Rabat. They have different ages and format (table 1), depending on the size of the related folios, and they are all made in paper support. Figure 1 exhibits the images of the four manuscripts.

Table 1. Description of the analyzed paper manuscripts.

Manuscripts	Format	Age (century)	Inks
M1	145 × 187 mm	19th	Black, blue, orange
M2	154 × 227 mm	17th	Black, orange, red
M3	140 × 195 mm	16th	Black, red
M4	160 × 250 mm	14th	Black, red

Fig. 1. Documents under study: (a) Manuscript (M1) dating back to the 19th century. (b) Manuscript (M2) dating back to the 17th century. (c) Manuscript (M3) dating back to the 16th century. (d) Manuscript (M4) dating back to the 14th century.

The content of the studied manuscripts is religious text inscribed in the Arabic language, with a combination of black, blue, orange and red ink. This was standard practice in ancient Arabic manuscripts, where black was used for the main body of the text and definition, while red, orange and blue were used to mark headings, important phrases or for highlights.

The manuscripts have been stored under controlled environment conditions provided by the library (23 °C and 50% relative humidity (RH)). The written area of the four manuscripts appeared in a quite good state of conservation, as no degradation signs were noticed for ink. Notwithstanding the initial visual inspection, the document M4 presents traces of a biological attack, while signs of humidity were observed in the sample M3 and M1.

Examinations were performed on the cellulosic support and on the inks originating from four Islamic illuminated manuscripts belonging to the Royal Library of Rabat.

Triaxial geometry EDXRF analysis

The paper support was analyzed directly using a spectrometer with orthogonal triaxial geometry between the side window X-ray tube (W, 100 kV, 80 mA max.), the secondary target (Mo), the sample and the detector. A nitrogen cooled Si(Li) with a 30 mm^2 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 [13]. 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 [14].

μ-EDXRF analysis

For ink characterization, paper support and inks were directly analyzed using the commercial Tornado M4® μ-EDXRF spectrometer from 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 mm^2 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.

Scanning electron microscopy (SEM)

Environmental scanning electron microscopy scans were obtained using a Quanta 200 MK2. This microscope is a high-resolution imaging equipment that does not require any sample coating or preparation. 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. SEM images have been obtained using the secondary electron (SE) detector at different magnifications.

X-ray diffraction (XRD)

XRD experiments were performed on paper collected samples using an X-ray diffractometer (X'Pert Pro model) operating with Cu Kα radiation ($\lambda = 1.5406$ Å). The current was adjusted to 30 mA. The voltage was increased to 40 kV. The reflection angle 2θ was in a range between 10° and 70°, it changed of 0.016° with a step of 40 s.

X-ray diffraction is an important experimental technique for phase identification and determination of crystalline structures. The crystallinity index (CrI) has been used to describe the relative amount of crystalline material in cellulose. The degree of crystallinity was calculated by the empirical method for a cellulosic fraction [15]:

$$CrI = ((I_{200} - I_{\mathrm{am}})/I_{200}) \times 100. \quad (1)$$

I_{200} is taken at a 2θ angle varying between 22° and 23° that corresponds to the maximum intensity of diffraction of crystalline cellulose, and I_{am} is taken at a 2θ angle between 18° and 19° where the intensity of diffraction of amorphous cellulose is at its minimum.

Results and discussion

Paper support: Cellulose matrix

The X-ray diffractograms of cellulosic support of four manuscript samples M1, M2, M3 and M4 are given in figs. 2(a) and (b). Table 2 summarizes the band position (2θ) and d-spacing of crystalline cellulose regions for the studied paper manuscripts.

Four crystalline peaks were detected in the XRD profiles of all samples (fig. 2(a)). The first one assigned to the (1^{-10}) crystallographic plane is located at $2\theta = 14.61°$–$14.92°$ reflection, the second related to (110) crystallographic plane is detected at $2\theta = 16.36°$–$16.55°$ reflection, the third associated to the (200) crystallographic plane is located at $2\theta = 22.64°$–$22.82°$ reflection, and the fourth attributed to the (040) crystallographic plane of cellulose I is detected at $2\theta = 34.05°$–$34.64°$ reflection [16–19].

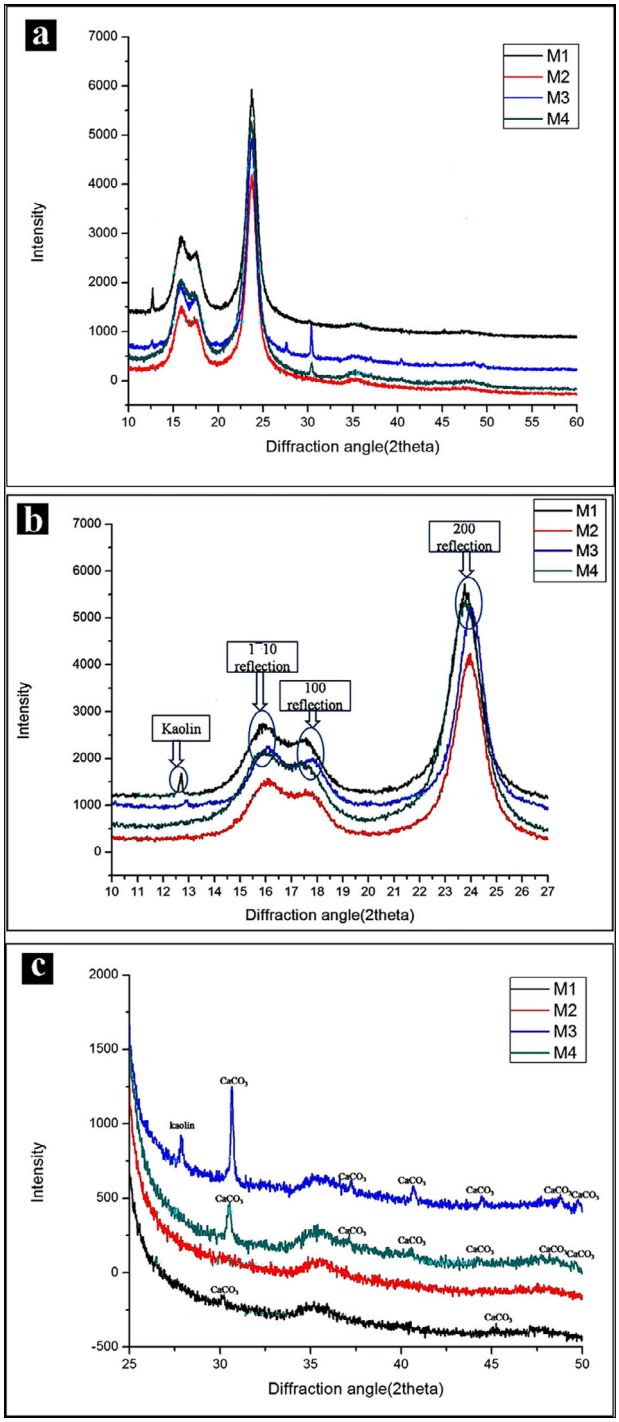

Fig. 2. X-ray diffractometry profiles of paper samples M1, M2, M3 and M4; diffractogram details: (a) angular range 10° and 65° 2θ; (b) angular range between 10° and 27° 2θ; (c) angular range between 25° and 50° 2θ.

Table 2. Band position (2θ) and d-spacing of crystalline cellulose regions for the paper manuscripts studied.

	1^{-10}		110		200		040	
Paper manuscripts	2θ	d (nm)	2θ	d (nm)	2θ	d (nm)	2θ	d (nm)
M1 (19th century)	14.92	0.593	16.55	0.535	22.82	0.3893	34.57	0.2591
M2 (17th century)	14.74	0.600	16.36	0.541	22.64	0.3924	34.41	0.2605
M3 (16th century)	14.61	0.605	16.55	0.534	22.68	0.3917	34.05	0.2633
M4 (14th century)	14.89	0.594	16.55	0.535	22.77	0.3901	34.64	0.2587

Table 3. Parameters obtained from the XRD analysis of the samples under study.

Paper samples	CrI (%)	Z values
M1	86.36	−27.62
M2	84.14	−21.18
M3	86.66	−6.4
M4	83.9	−25.92

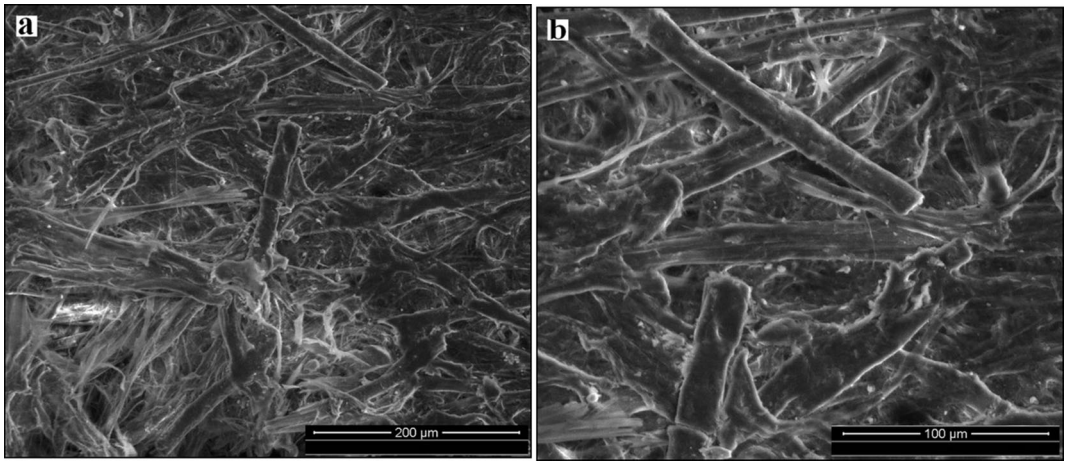

Fig. 3. SEM-SE micrographs of the cellulosic support of the manuscript M1.

All samples have a similar diffractogram related to the content of the cellulosic material, but they differ in terms of peak intensities of the amorphous and crystalline fraction of cellulose. Figure 2(b) shows an important change at the I_{200} peak related to the (200) crystallographic plane, where M3 has the highest peak intensity and M2 has the lowest one. The intensity of (200) peak for M3 is justified by its crystallinity degree (86.66%) as shown in table 3.

The crystallinity degree of the cellulose matrix can be related to the degradation level of cellulose. It is well known that the degradation pathways first occur in the amorphous phase of cellulose, and only in a second stage, the crystalline phase is attacked [20]. Therefore, values of CrI lower than those typical of cellulose (more than 80%) indicate a degraded material or a paper made of low-quality cellulose fibers.

The CrI values corresponding to the analyzed papers are displayed in table 3. The CrI values of all samples are varying between 83.9% and 86.66%. These results confirm that the samples were made of a high-quality paper material [11].

Cellulose I contains both crystalline (up to 80% depending on the source) and amorphous regions [21]. In the crystalline phase two polymorphous forms of native cellulose, namely I_α and I_β, are present [22]. The relative amount of the two polymorphs depends on the botanical origin of the cellulose. By employing discriminant analysis, it is possible to categorize cellulose between I_α or I_β dominant type [23]. The function (Z), which discriminates between I_α and I_β, is given by Wada and Okano [24]:

$$Z = 1693d1 - 902d2 - 549, \tag{2}$$

$d1$ is the d-spacing for the (1_10) crystallographic plane and $d2$ is the d-spacing for the (110) plane. Both distances $d1$ and $d2$ must be calculated in nanometers.

The triclinic structure of native cellulose I_α is characterised by $Z > 0$, while $Z < 0$ indicates the presence of I_β cellulose dominant type (monoclinic structure dominates) [25].

The Z values of all samples are ranging between −27.62 and −6.4 (table 3). These results confirm that all the papers are I_β type cellulose I.

Observation carried out by scanning electron microscopy (SEM) helped to have a better knowledge of the typical morphology of paper, highlighting some effects of the degradation process [26,27]. Micrographs presented in figs. 3–6 present the surface morphology of documents M1–M4, respectively.

The observation of the surface of the paper of sample M1 reproduced in fig. 3 shows that the whole chains of the cellulosic fibers bundle together randomly, contributing to a heterogeneous network structure. It is worth to note that some fibers are broken.

The micrographs in fig. 4(a) show that the surface of this sample is described by a typical structure constituted by long fibrous bundles which, have different shapes and sizes. Figure 4(b) shows some breakage of the cellulosic structure of the selected paper.

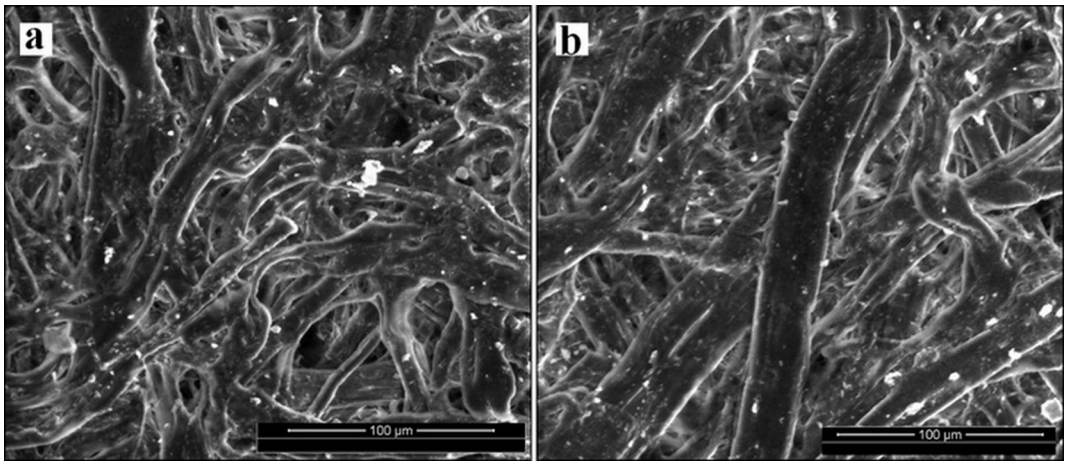

Fig. 4. SEM-SE micrographs of the cellulosic support of the manuscript M2.

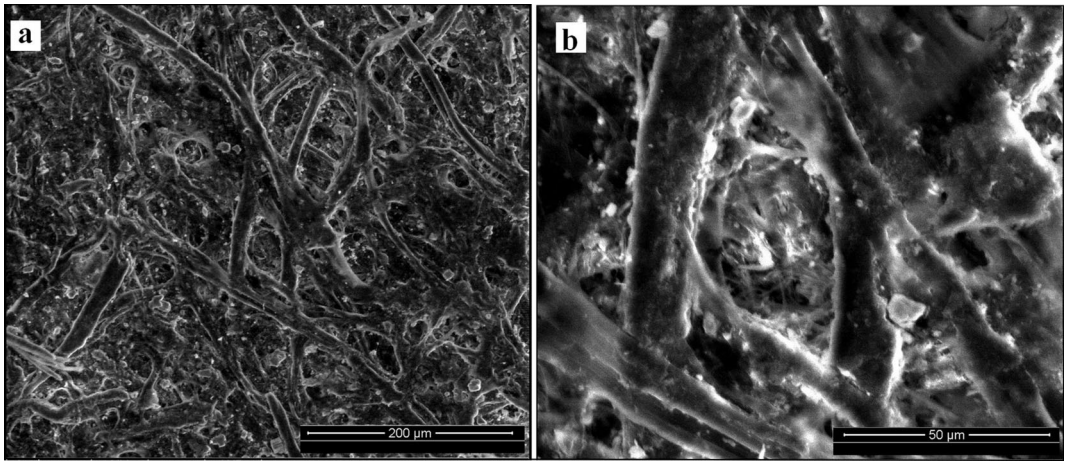

Fig. 5. SEM-SE micrographs of the cellulosic support of the manuscript M3.

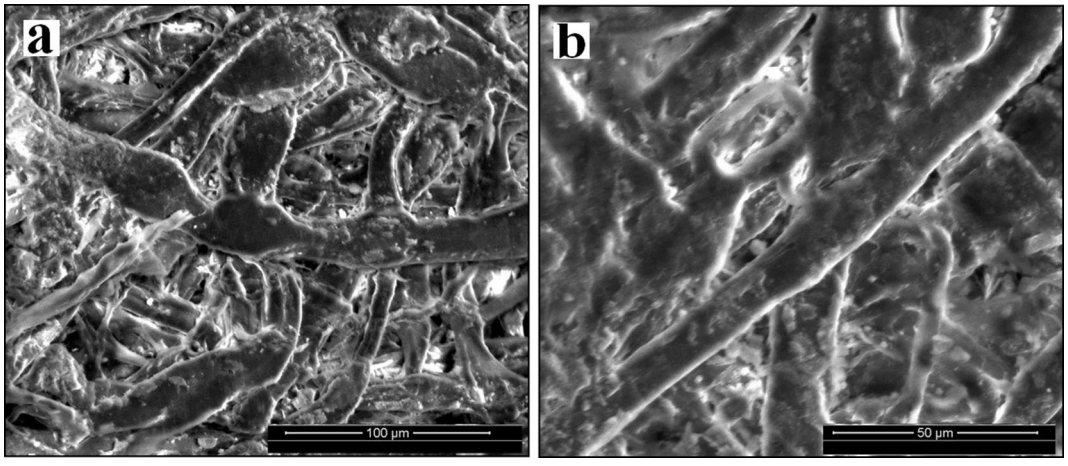

Fig. 6. SEM-SE micrographs of the cellulosic support of the manuscript M4.

The micrographs presented in fig. 5 evidence that the cellulose structure of M3 is of the fibrous type in the form of a chain of irregular orientation with an irregular porosity. No breakage of the cellulosic structure of the selected paper was observed.

The structure of the paper M4 is formed by vascular bundles running in a perpendicular direction (fig. 6). A closer look at the microfibril surface shows that no significant degradation of the cellulosic fibers and no broken fibers can be noticed. Moreover, the paper seems to be in a good condition.

Table 4. Mean element content and standard deviation ($\mu g \cdot g^{-1}$) obtained with the triaxial geometry setup.

Elements	M1 (19th century)	M2 (17th century)	M3 (16th century)	M4 (14th century)
S	1185 ± 120	1645 ± 165	1620 ± 160	1530 ± 150
Cl	2940 ± 300	1770 ± 180	6390 ± 630	6280 ± 630
K	1230 ± 120	1360 ± 140	3400 ± 340	1560 ± 160
Ca	2010 ± 200	2260 ± 230	26400 ± 2640	16100 ± 1610

Paper support: fillers and sizing agents

In fig. 2, X-Ray diffractograms of the cellulosic support of the studied samples show, not only the characteristic peaks of cellulose, but also those corresponding to the inorganic composition of the paper support —the fillers (fig. 2(c)). These mineral components were admixed with the cellulose fibers before the paper was made. By filling the voids between the fibers, it increased the weight of the sheet and imparted optical and writing properties to the paper [28].

Figure 2(c) shows the presence of a common mineral filler, calcium carbonate ($CaCO_3$). It presents the characteristic peaks at $2\theta = 29.24°$ and $44.32°$ in the manuscript M1, while it was identified, in the manuscripts M3 and M4, with the characteristic diffraction peaks at $2\theta = 29.24°$, $36.05°$, $39.46°$, $43.25°$, $47.60°$ and $48.61°$ [12,29]. This result explains the presence of calcium in the three manuscripts obtained by triaxial geometry EDXRF spectrometry (table 4), and possibly the presence of light particles immersed in the fiber matrix of the manuscripts supports observed by SEM (figs. 3(b), 4(b) and 5(b)). The presence of calcium carbonate could have contributed to the good condition of the cellulosic support of M1, M3 and M4.

Concerning M2, XRD results have not confirmed the presence of $CaCO_3$ in this sample. However, EDXRF results (table 4), have revealed the presence of calcium in the manuscript support.

It is interesting to note that the intensity of calcite peaks (fig. 2(c)) in the oldest manuscript M4 (aged the 14th century) and in M3 (dating to the 16th century) is higher than that in the most recent paper M1, aged the 19th century (fig. 2(b)). This can be explained by the high content of calcium that has been used, providing an alkaline reserve that guarantees the longest life to papers [13]. Calcite was the most frequent filler used in the alkaline paper manufacturing process and as a sizing agent. Besides improving several important paper characteristics, such as smoothness, brightness, opacity, and affinity for ink. It also reduces paper acidity, prolonging paper life [12,28,30].

It is worth mentioning that the peaks located at $2\theta = 11.67°$ and $26.68°$ in the diffractogram of the manuscripts M3 (figs. 2(b) and (c)) are presumably due to Kaolin [$Al_2Si_2O_5(OH)_2$] [11], another filler used in the papermaking process. Relatively high levels of fillers are shown in the M3 SEM microphotographs (figs. 5(a) and (b)), in which the light particles immersed in the cellulose matrix may be related to the presence of calcite and kaolin.

The presence of a peak located at $2\theta = 11.74°$ in the diffractogram of M1 (fig. 2(a)) indicates that probably a third filler was used. Nevertheless, we were not able to identify it.

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 [30]. The presence of elemental sulphur 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 [31].

Black inks

All manuscripts are written in iron-based ink. Besides iron, sulphur was also identified in all documents. The overlap distribution of Fe-Kα and S-Kα at M1, M3 and M4 could indicate the presence of vitriol used to prepare iron gall inks (figs. 7–9). The vitriol was extracted from different mines and by different techniques. The other metals, like copper (M1 and M4), manganese (M3 and M4) and zinc (M3), might have arisen from iron sulphate contamination [32]. M3 contains a remarkable high quantity of copper, relative to iron, suggesting that copper vitriol could have been added to the black ink (fig. 8). This form of vitriol is reported to be well known and used in ancient times [33]. The presence of potassium in all the black inks can indicate the use of the gum Arabic as a binding media, preventing the precipitation of the water-insoluble black ferric gallic pigment [8,31].

Blue inks

Blue ink was only used in the 19th century manuscript (M1). The high intensity of copper lines indicates the use of azurite (fig. 7), which is a local pigment. Barium and lead L lines are also evident in the μ-EDXRF spectrum of this ink. Lead white, combined with azurite, has been previously detected by Roger *et al.* [8] in light blues present in the 13th and 16th century Moroccan manuscripts. In the paint, barium sulphate is almost transparent and is used as a filler pigment replacing partly the need of the most expensive part of ink, colored pigment, and hence reducing the cost of the ink. Barium sulphate was also used in paint to modify the ink consistency [34].

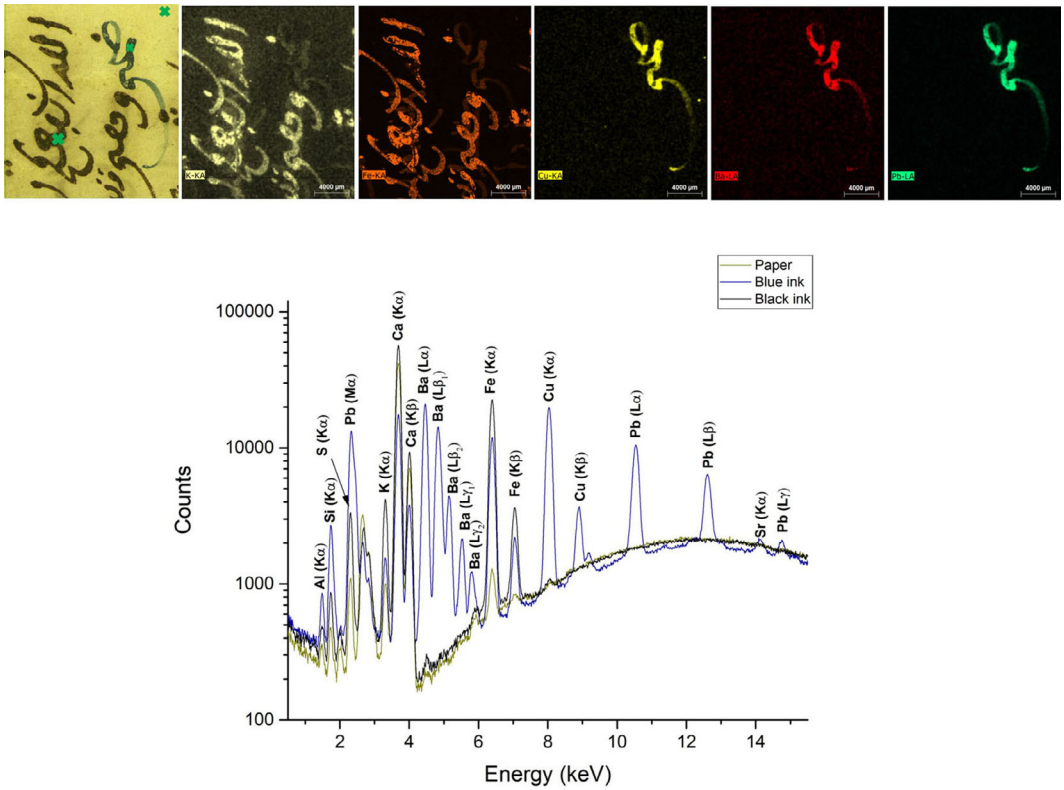

Fig. 7. Distribution of K, Fe, Cu, Ba and Pb obtained by μ-EDXRF at black and blue ink from manuscript M1. μ-EDXRF spectra refer to the points of analysis presented at the microphotograph.

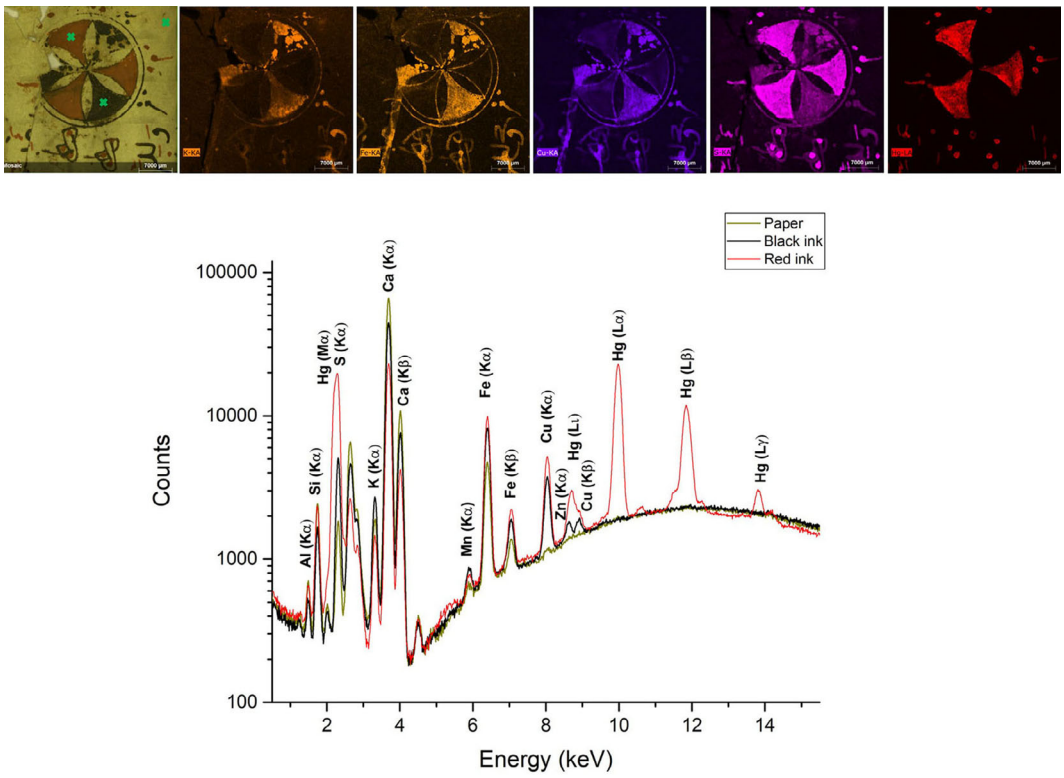

Fig. 8. Distribution of K, Fe, Cu, S and Hg obtained by μ-EDXRF at black and red ink from manuscript M3. μ-EDXRF spectra refer to the points of analysis presented at the microphotograph.

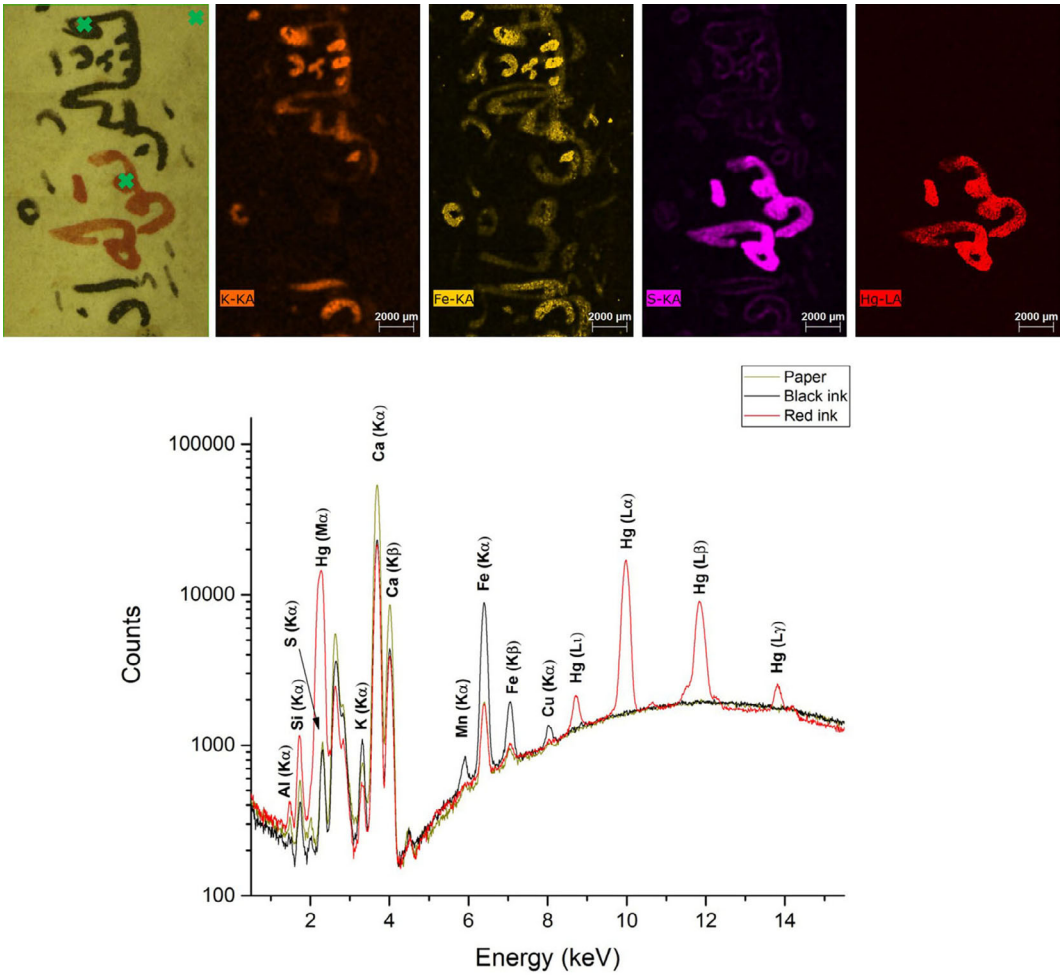

Fig. 9. Distribution of K, Fe, S and Hg obtained by μ-EDXRF at black and red ink from manuscript M4. μ-EDXRF spectra refer to the points of analysis presented at the microphotograph.

Red inks

Red ink can be observed in M2, M3 and M4 manuscripts. The presence of mercury detected by μ-EDXRF in these inks makes clear the use of red cinnabar —mercuric sulphide (figs. 8–10).

Orange inks

Orange inks were only observed in M1 and M2 manuscripts. The presence of lead in M1 could indicate the use of minium, a red lead oxide. While the presence of arsenic in M2 could be related to the use of orpiment, a yellow arsenic sulphide that, in combination with an organic red dye, could reproduce the orange color (fig. 10).

Conclusions

In this research, a multi-analytical study comprising triaxial geometry EDXRF, μ-EDXRF, XRD and SEM was carried out to characterize the inorganic components in cellulosic support (cellulose matrix and fillers), and the mineral composition of inks in the four manuscripts dating back to the 14th, 16th, 17th and 19th centuries.

X-ray diffraction has proven to be a suitable technique to elucidate the cellulose main features, to identify the inorganic composition of the paper and to study the crystallinity of samples. XRD results of the cellulose matrix revealed that all samples are I_β cellulose type, characterized by high values of crystallinity index CrI of the cellulose matrix. This confirms that the manuscripts were made of a high quality of the paper material and they are in a good state of conservation. Indeed, sample M3, dated to the 16th century, displayed the highest value of CrI index ($CrI = 86.66\%$). Concerning the presence of the fillers in the cellulosic support, XRD analysis results confirm the presence of calcite ($CaCO_3$) in all samples except for M2. However, the results obtained with the triaxial geometry EDXRF setup show Ca in all samples M1, M2, M3 and M4.

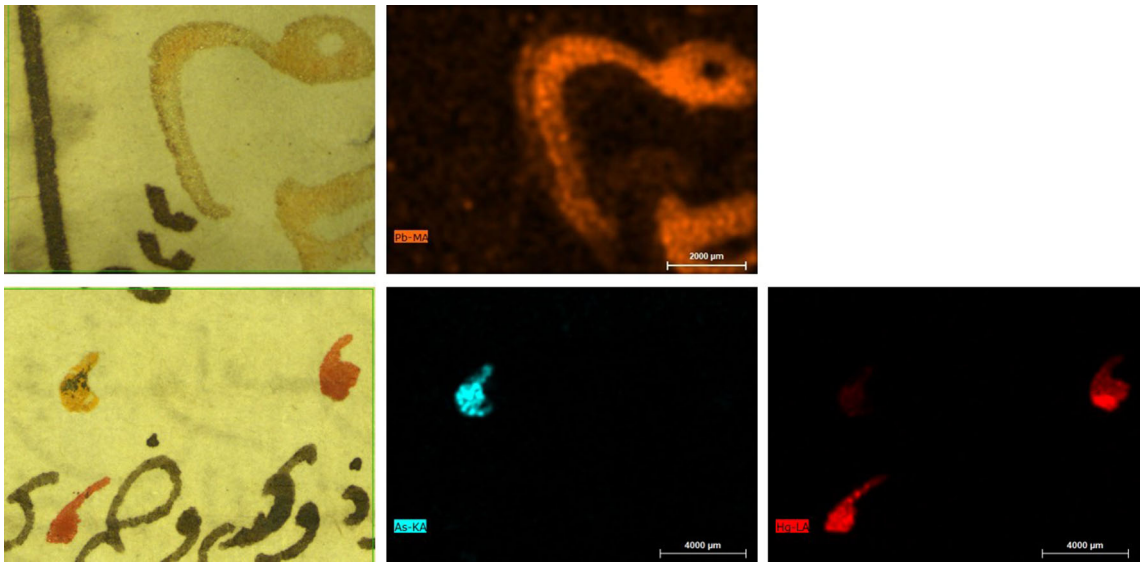

Fig. 10. Micro-EDXRF distribution of Pb and As at orange inks from manuscript M1 and M2, respectively. Mercury was found at the red ink from M2.

Observations carried out by SEM helped to have a better knowledge of the typical morphology of paper highlighting some effects of the degradation process. In fact, SEM observations revealed that the papers under study were in a good state of conservation as confirmed by the preservation of cellulose fibers.

The μ-EDXRF analysis provided the elemental distribution in writing and colouring materials enabling inks and pigments identification. Results revealed that scribes and illuminators used a large palette of colouring materials originating from minerals: the analysis in the black area revealed the presence of iron and sulphur, confirming the use of the iron-based ink in the written body text of all manuscripts. In addition to iron, the μ-EDXRF analysis revealed the presence of other metals like copper (M1 and M4), manganese (M4), zinc (M3) and potassium in all samples. These results indicate that the inks were differently prepared and sometimes differently applied.

μ-EDXRF results confirm the use of the mineral azurite for the blue ink in the manuscript M1 (dated the 19th century), while the red cinnabar mercuric sulphide was used for the red ink in the three samples M2, M4 and M3, and finally a combination of a possible organic red dye and a yellow arsenic sulphide reproduce the orange colour in M1 and M2 manuscripts. The use of barium in addition to copper blue was recorded for the first time in Moroccan manuscripts.

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