

*Full Length Research Paper*

# Scientific investigations on paper and writing materials of Mali: A pilot study

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**The investigation of physical properties and chemical composition generates data important for answering cultural-historical questions that cannot be solved by historical and philological methods alone. Due to technological developments, technical diagnostics in art and culture are in ever-greater demand in such fields of transdisciplinary research. Natural sciences play auxiliary role in the studies of manuscripts. The success of their contribution depends strongly on the formulation of the question, the choice of the methods to obtain the requested answer, and appropriate reference databases. First, report was given on the measurements performed on local raw materials, such as, plants, minerals and animals, which constitute the reference session. Then, the first results of the scientific analysis of several fragments from the Malian manuscript collections were present.**

**Key words:** Manuscripts, inks, colorants, scientific investigation, non-destructive testing.

## INTRODUCTION

Archaeological and art historical research often concerns the questions of origin, dating or attribution of cultural objects. Stylistic and art historical considerations in combination with extant technological treatises and recipes can answer many questions, but sometimes the analysis of the physical properties and the chemical composition of the artefacts is essential. Determination of chemical composition of cultural objects is also crucial for their conservation.

The collections in Bamako contain a vast number of manuscripts that were written and decorated with different inks and colourants on paper (Russo, 2017). Dating of paper can be roughly made through the key

events of paper production. The heyday of Arabic paper production was between the 8<sup>th</sup> and the 13<sup>th</sup> century. After that, the centre of paper production shifted to Europe, especially Italy, although Arabic paper was still produced in the Middle East until the end of 15<sup>th</sup> century and until the 19<sup>th</sup> century in Central Asia (Loveday, 2001). Meanwhile many changes, concerning both process and materials, were introduced in Europe, leading to the industrial production of paper that started in the 18<sup>th</sup> century in Central Europe. Among the important innovations counted were the appearance of Hollander beater (1680), the introduction of the wove mould-covering and the increased use of cotton (second half of

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**Figure 1.** Koronifin (*Vitex Chrysocarpa*, left), Hibiscus (*Hibiscus Sabdariffa*, middle), and Laterite (Hematite, right); ©Eva Brozowsky, CSMC.

the 18<sup>th</sup> century). Also included are the invention of the paper machine (1798), the Fourdrinier wire webs and cylindrical forming vats (1806), the mass gluing of the pulp before scooping (also known as internal sizing) and application of rosin sizing (1807). Lastly, the use of ground wood as a source of fibers (first attempts in 1800, patented by Keller in 1840) (Hunter 1974).

Since it is assumed that the manuscripts were preferentially produced locally, in Djenné, Timbuktu or Kayes it was also assumed that the manufacture of the writing materials was based on local plants, minerals and animals (Haïdara, 2015). In addition, inks might contain a wide range of components and impurities due to individual recipes and the natural origin of raw materials. Therefore, a better understanding of the production processes of the local manuscripts requires the use of analytic techniques for characterization of writing materials.

A particular requirement for the scientific investigation of the manuscripts – also in Bamako – is the use of mobile equipment that employs non-destructive or micro-invasive techniques. In accordance to Lahanier et al., (1986), the ideal procedure for analysing art, historical, or archaeological objects should be non-destructive respecting the physical integrity of the object, but also fast to analyse large numbers of similar objects or to investigate a single object at various locations. In addition, the measurements should be universal to analyse many manuscripts and related objects of various shapes and dimensions, as well as versatility, permitting acquisition of average compositional information but also allowing local analysis of small areas. There are several analytical methods commonly used in the non-destructive, mobile and “multi-instrumental” approach for manuscript investigation, which embraces microscopy, elemental analysis, and chemical characterization. However, appropriate reference materials and databases are essential for the coherent interpretation of the analytic results.

## SAMPLES

### Collection and revision of recipes from oral sources

In the first stage of the study, the recipes and plant materials to be included into the ink and dye database were collected in Bamako and in Djenné. Since no written records for ink production were available, the ink recipes were compiled in interviews with local Marabouts and scribes of Djenné. Overall, 30 basic recipes were obtained for colorants and inks used to gather samples that amount to 80 specimens. The recipes were sorted according to the ink types (soot, tannin, iron-gall or iron-tannin dye or pigment, mixed), according to the production method (by sun maceration, by cooking, by squeezing, by pounding), and according to the secondary ingredients (such as, binder, colour enhancer). Following this step, the necessary ingredients to procure the local plants and minerals were identified. The reference set includes different leaves (such as, *Acacia senegalensis*, *Indigofera tinctoria* / *Indigofera arrecta*), flowers (such as, Hibiscus), and fruits (such as, *Cola cordifolia* / *Cola nitida*, Zafrane (local name), and *Acacia senegalensis*). It also includes bark (such as, *Acacia senegalensis*, Bari (local name), *Vitex Chrysocarpa* = Koronifin (local name), Pegu (local name), resins (such as, *Acacia senegalensis*) as well as minerals (such as, Laterite), and metals (such as, Gold) (Forgues and Bailleul, 2009). Figure 1 shows selected raw materials.

### Reference sample preparation

Using the collection of the recipes and materials, different dummy inks were produced and were applied to standardized paper as shown in Figure 2. Ink production included extraction of the different plants using water or potassium carbonate solutions. First, the plants (flowers, fruits, bark, nuts, seeds, and leaves) were ground; the



Figure 2. Set of reference samples manufactured with self-made inks; ©Eva Brozowsky, CSMC.

resulting powders were boiled for 30 min to 1 h at 100°C in a bath consisting of purified water or potassium carbonate (15%). The coloured extracts were filtered with Whatman™ filter paper and dried. Finally, the plant extracts and/or minerals were mixed with binders (such as, gum Arabic) that were produced separately.

#### METHODS OF SCIENTIFIC ANALYSIS

The reference samples were investigated optically (microscopy, Figure 3), with ultraviolet (UV) and near infrared (NIR) reflectography (Figure 4), visible reflectance spectroscopy (VIS, Figure 5), Fourier transform infrared spectroscopy (FTIR-ATR, Figure 6), micro-Raman- spectroscopy (Figure 7), and micro- X-ray fluorescence analysis (XRF, Figure 8).

For the studies of the original manuscripts, the systematic non-destructive investigation protocol developed in a collaborative effort between the Bundesanstalt für Materialforschung und -prüfung (BAM) and the Centre for the Study of Manuscript Cultures (CSMC) were followed (Rabin 2014; Hahn and Nöller, 2014). Following this protocol microscopy and FTIR were used to investigate the writing supports to determine the type of paper used in each manuscript. After this step, each manuscript was subjected to a reflectographic screening with ultraviolet (UV), white, and near-infrared illumination (NIR) to obtain a preliminary grouping of the black writing inks. This sorting was supplemented by XRF analysis to obtain the relative concentration of metals in the iron-gall inks. The metal composition was then used to compare the inks, that is, to identify the individual ink recipes. The composition of the coloured inks was identified with the help of visible reflectance spectroscopy in conjunction with XRF.

#### Light Microscopy

Classification of different ink types is carried out with microscope (Keyence VHX-5000, at magnification: x 200). In contrast to the pure plant ink (Figure 3, left) and the carbon ink (Figure 3, middle) the iron gall ink shows brown haloes around the ink stroke (Figure

3, right) indicating the presence of tannins. The distinction of different black drawing materials is the starting point for the development of successful restoration or conservation concepts.

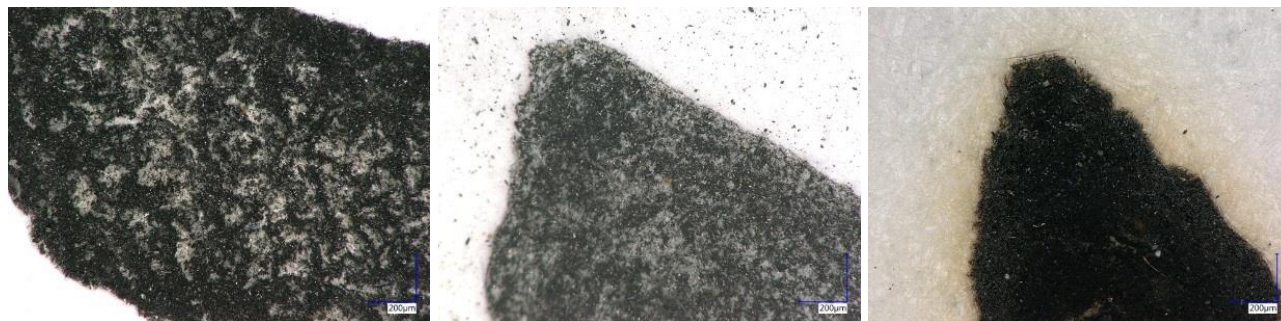
#### Reflectography

In general, infrared (IR) reflectography is used to reveal underdrawings in paintings. The method is based on the fact that certain materials (such as, pigments) absorb very little infrared radiation in the spectral range between 750 and 1500 nm (near infrared). Radiation incident on carbon-based underdrawings is strongly absorbed and becomes “visible” by means of appropriate cameras. In addition, the method provides an appropriate technique to distinguish between carbon-based (carbon ink) and non- carbon-based (iron gall ink, plant ink) drawing and writing materials (Mrusek et al., 1995).

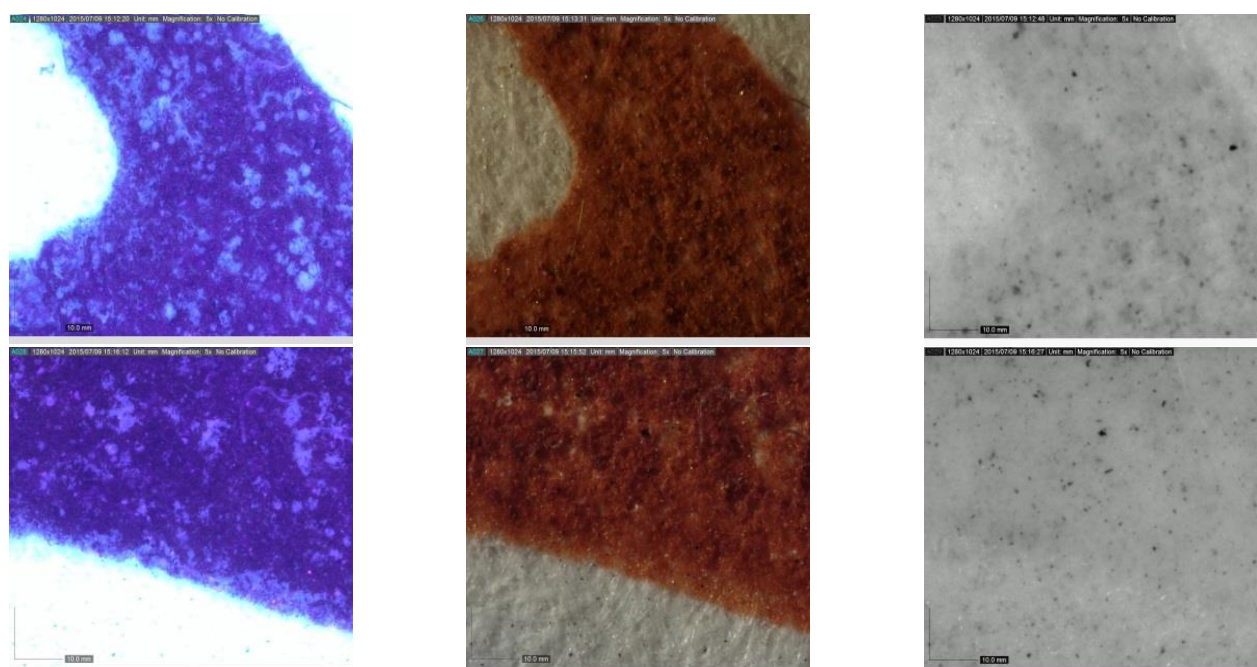
Ultraviolet (UV) photography is a convenient tool to visualize older compositions, hidden signatures, and retouched areas of works of art (Hain et al., 2003). UV fluorescence is a kind of luminescence. A substance (such as, binding material) irradiated by UV light emits light in the visible range of colours. Under UV light, old paint or varnish layers emit more fluorescent light than “modern” materials do. Retouched or re- stored areas appear darker under investigation. UV reflectography is a convenient tool to visualize text fragments that became discoloured over time. Furthermore, it can be used to analyse the binding media used for paper preparation. The measurements were carried out with a three-color USB microscope (Dino-Lite AD413T-I2V, at magnification: x 50), that is commonly useful in determining the ink typology and surface morphology. The microscope possesses in-built LED illumination at 395 and 930 nm and an external white light source. In the case, of these dummy samples, the microscope was used to build an atlas of typical images as a part of the database. An example of such an entry in the database can be seen in Figure 4.

#### Visible reflectance spectroscopy

By means of a spectral photometer, the colour value of a colorant can be quantitatively determined based on its reflective spectrum in the range of visible light (380 to 730 nm). With this surface method,



**Figure 3.** Microscopic images of plant ink (Koronifin, left), carbon ink (lamp black, middle) and iron gall ink (tannin: bark of *Acacia Senegalensis*, right).



**Figure 4.** From left to right UV/VIS/NIR-micrographs of Laterite (upper row) and Zafrane (bottom row). The NIR- reflectography (right column) shows the difference between both red colorants: the dye Zafrane completely disappears at 940 nm whereas the pigment Laterite is still slight visible.

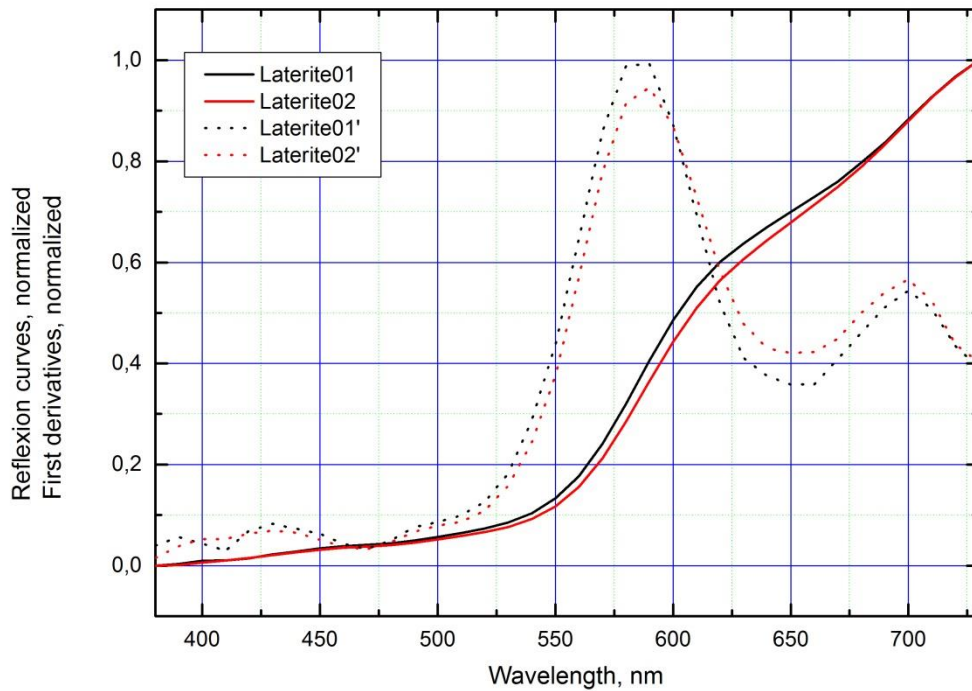
the sample to be examined is illuminated with visible light. The sample material interacts with the visible light by absorbing or reflecting it in a specific way, thereby appearing coloured. The reflected light characteristic of a specific pigment is measured with a photometer and recorded in the form of a characteristic reflection curve. This curve represents the correlation between the intensity of the reflected light and its wavelength. Comparison with a databank makes it possible to ascribe the pattern to a certain pigment or dye (Fuchs and Oltrogge, 1994). In the example below, the curves display characteristic features for a red colorant (Figure 5).

The examinations were carried out with the aid of the spectral photometer SPM 100 (Gretag Imaging AG company Regensdorf, Switzerland) equipped with a 3 mm sensor and 2W white light bulb.

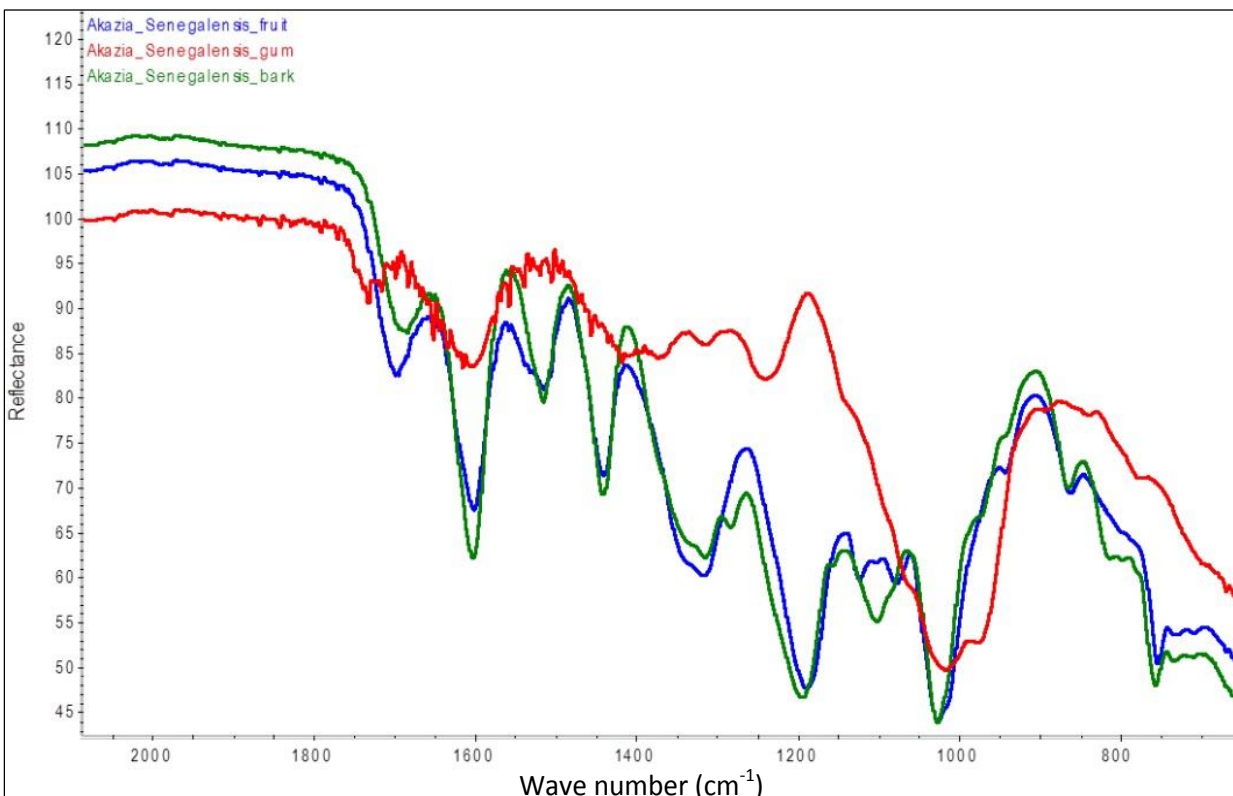
The measurements were conducted with 10 nm wavelength resolution and 0.5 sec illumination time.

#### Vibration spectroscopy (ATR-FTIR and Raman spectroscopy)

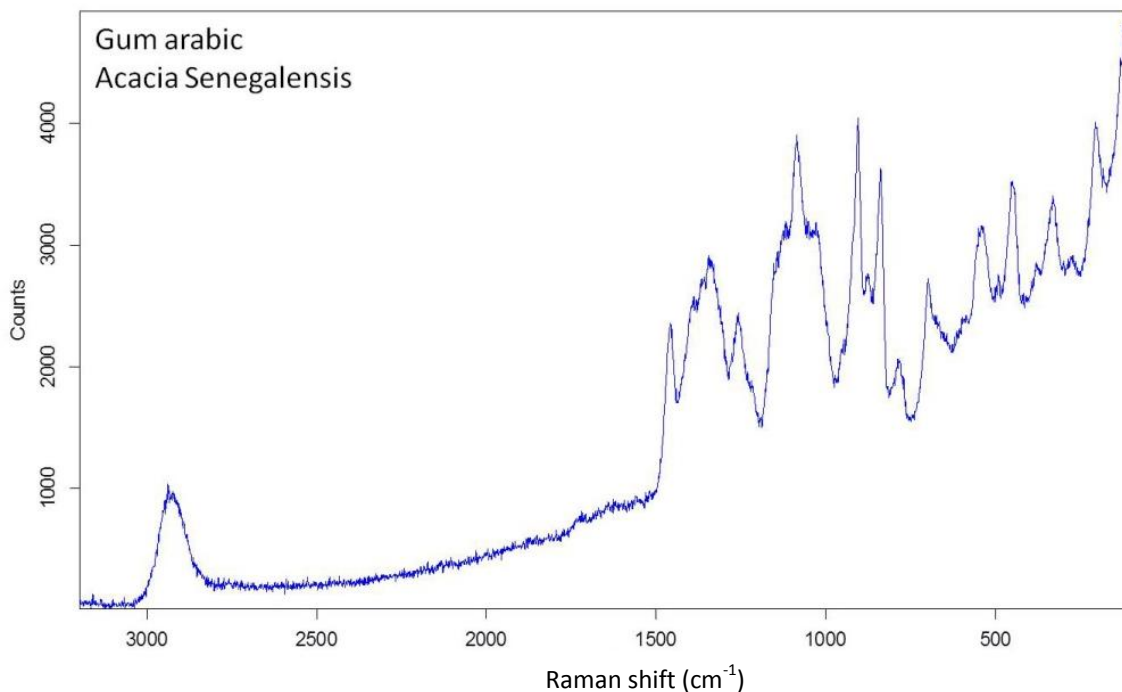
IR and Raman spectroscopy techniques are common methods to reveal the chemical composition of unknown assays. In the first, portions of IR light at characteristic frequencies are absorbed, leading to the identification of the corresponding molecules. In the second, which is named after its discoverer Chandrasekhara Venkata Raman, portions of UV, VIS, and NIR light are in elastically scattered to collect similar information. With the FTIR spectroscopy method used over the last 120 years, samples were usually measured in transition mode, which means that small samples had to be taken from an object. Recently, non-destructive methods have been developed to study the surfaces of various objects. The miniaturization of IR sources and detectors has enabled the development of a new generation of portable spectrometers that allow handheld investigation in a diffuse reflection mode or in ATR



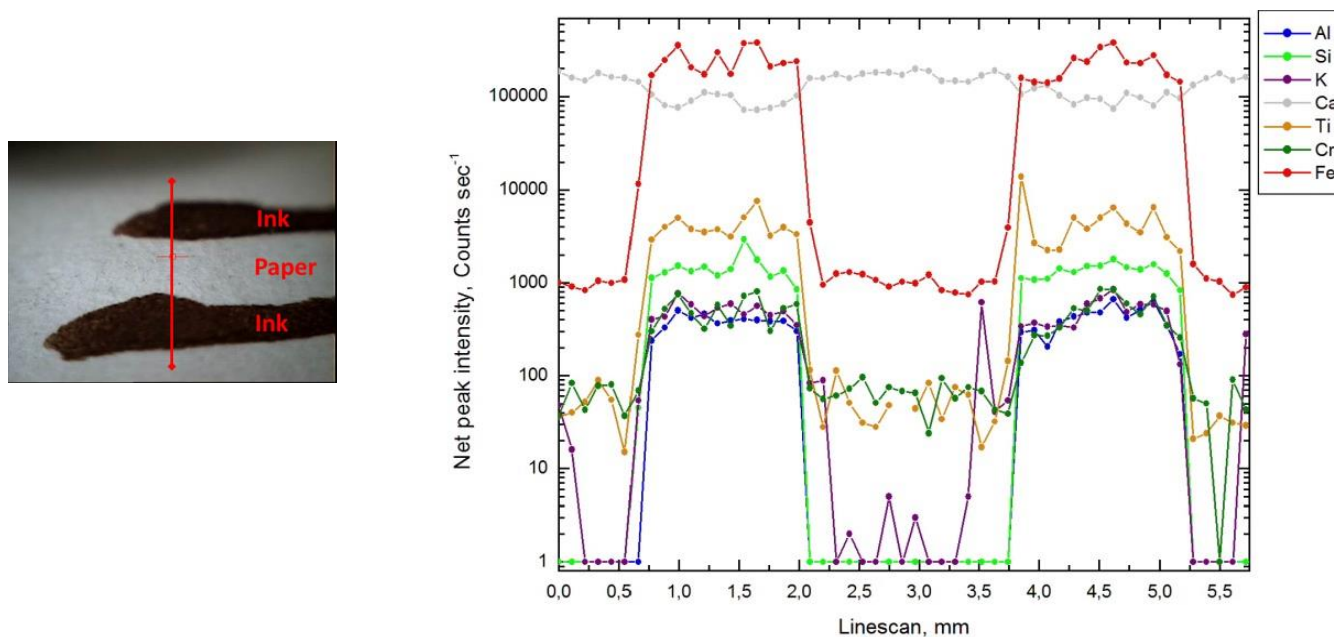
**Figure 5.** Normalized reflexion curves of the of the Laterite samples 1 and 2 (red and black solid lines), the corresponding derivatives (dotted lines).



**Figure 6.** Comparison of FTIR-ATR spectra of gum (red), fruit (blue), and bark (green) from Acacia Senegalensis.



**Figure 7.** Raman spectrum of gum Arabic (resin of *Acacia Senegalensis*); characteristic bands of carbohydrates between  $1500\text{ cm}^{-1}$  and  $800\text{ cm}^{-1}$  lead to unequivocal identification of the gums.



**Figure 8.** XRF line scan of two red Laterite ink strokes. Note the logarithmic scale of the y-axis. The main colorant is iron oxide (such as, hematite,  $\text{Fe}_2\text{O}_3$ ). The presence of characteristic traces of aluminium (Al), silicone (Si), titanium (Ti), chrome (Cr) and potassium (K) reveals the mineral nature of the raw material.

(attenuated total reflection) mode. FTIR spectra were collected with the Exoscan spectrometer (A2 Technologies) in ATR modus (Marengo et al., 2005). Measurements were performed in the spectral range between  $600$  and  $4000\text{ cm}^{-1}$  with a spectral resolution of  $4\text{ cm}^{-1}$ . 500 scans are co-added per spectrum.

In the example presented in Figure 6, different chemical composition of the gum of the *Acacia Senegalensis* is reflected in the IR spectrum, which is distinctly different from those of the fruit and the bark of the same tree. Raman spectroscopy is a technique that relies on the scattering of monochromatic light in the visible,

near infrared and near-ultraviolet range. It has proved to be a specifically powerful tool for identifying inorganic as well as organic materials. In the field of scientific manuscript analysis, it is now routinely used to identify inks, dyes and pigments, whose spectra are tabulated (such as, [www.irug.org](http://www.irug.org)).

The inVia™ Raman spectrometer has been specially adapted for the study of objects in the field of Cultural Heritage. Instead of a microscope, it is equipped with two fibre optics probes connected to lasers operating at 530 and 785 nm, respectively. The probes are connected to a camera to position the object and a CCD camera for signal registration. Measurements were carried out with 785 nm laser line, a x 50 lens and an output power of 5 mW in the spectral range 100-3600 cm<sup>-1</sup> with a spectral resolution of 4 cm<sup>-1</sup>. Three hundred scans were co-added per spectrum collected with 20 exposure.

### X-Ray fluorescence (XRF) spectroscopy

After classification of the writing materials using microscopy, reflectography or chemical analysis with vibrational spectroscopy, it was asked whether the script was executed with one or more carbon or pigment ink. Thus, the next step is the analysis of possible trace elements in the writing inks. In addition to colorants and binders, writing inks contain secondary components, such as salts of the elements potassium, calcium, copper, iron, manganese, or aluminium, among others. The varying composition of these different components is a characteristic property of writing inks and makes possible their exact determination.

Ageing phenomena have no influence on the applied XRF, because even if the chemical composition of the binder and the colorants may change due to chemical corrosion processes that alter the organic material, the proportion of metal components, that is, the elemental composition, remains the same. To estimate the presence and the real amount of trace elements, line scans with XRF were performed. The XRF spectrometer ARTAX (Bruker GmbH) is well known in the field of cultural heritage and belongs to standard equipment in the majority of large museums. It has a measuring spot size of 70 µm diameter, a CCD camera for sample positioning and an electrothermally cooled Xflash detector (SDD, area: 30 mm<sup>2</sup>) with an energy resolution of <150 eV at 10 kcps. XYZ motors that allow for spot measurements as well as line operate the movable probe and small area scans. Open helium purging in the excitation and detection paths allows for detection of light elements (Z ≥ 11). All measurements are made using a 30 W low-power Mo tube, operating at 50 kV and 600 µA, and with an acquisition time of 10 - 100 s (live time). The mobile XRF probe moves over the object at a distance of 5 mm and stops for the duration of a single measurement. A line scan consists of several single measurements along a chosen line.

In the example shown in Figure 8 left image shows two strokes made with Laterite ink and a corresponding line scan that traverses the strokes. The graphics on the right presents the net peak intensities extracted from each single measurement as a function of distance. The first 6 measurements present the elemental composition of the paper, in which only element calcium (Ca) has high intensity (grey solid circles). The intensities of all other elements that could be detected start growing only when, line scan reaches the inked area. The iron signal (Fe, red circles) grows extremely quickly and becomes higher than that of Ca once the scan reached the ink. It drops again when the scan leaves the ink to quickly grow once again when the second stroke is reached. The signals of all other elements that correlate with the ink, aluminium (Al), silicone (Si), titanium (Ti), chrome (Cr) and potassium (K), also grow and fall but always stay at least two orders of magnitude below that of the iron in the inked area. This behaviour reflects the mineral nature of the colourant used here: natural iron oxide with its

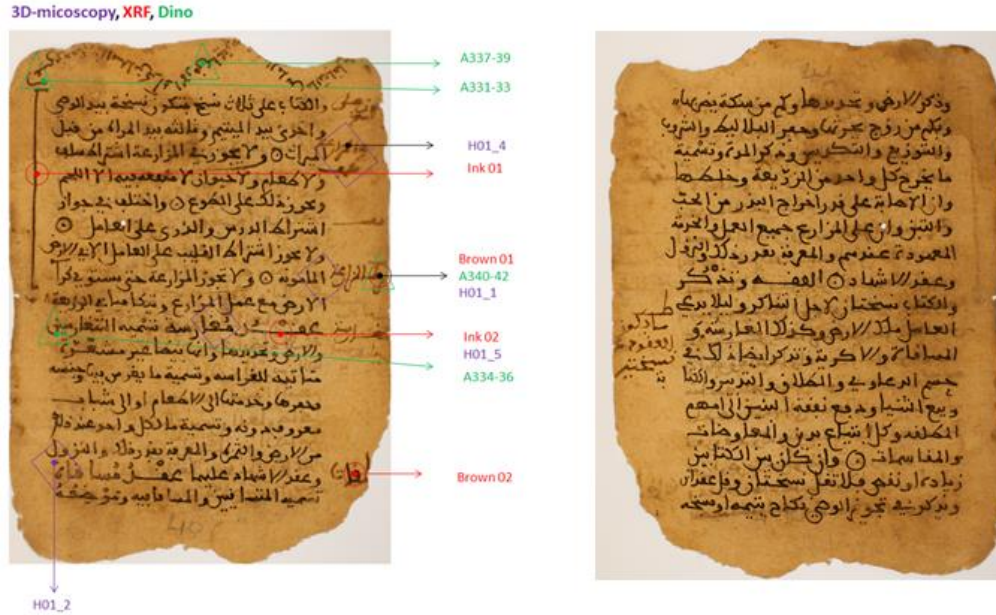
contaminants. The type and relative intensity of the contamination are very helpful in the provenance studies since they are specific for the natural mineral deposits (Nöller, 2012).

Note that the intensity of Ca drops slightly in the inked area. This does not mean that paper has less Ca in the inked area but reflect the fact that the thick layer of the ink absorbs some of the signal of the Ca fluorescence.

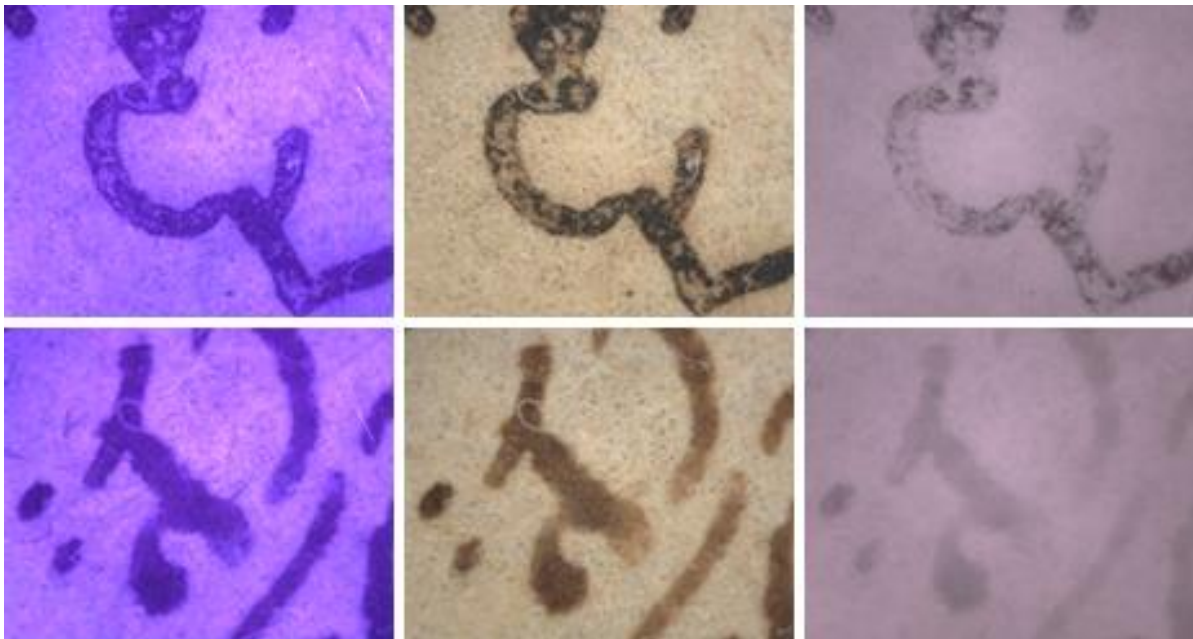
## RESULTS AND DISCUSSION

**Kitāb al-wathāiq, Abū Ishāq Ibrāhīm b. ʿAbd al-Rahmān al-Gharnātī (751/1350), Figures 9a-9e.** Figure 9a shows an example of the documentation of the tests conducted on the inks of the recto side of the fragment under investigation. Individual tests are color-coded: the arrows indicate the spot at which a measurement was conducted and the corresponding file name. In this case, a heterogeneous mixture of carbon and iron-gall ink in the main text was detected, whereas the comments were executed in pure iron-gall inks. Figure 9b demonstrates the optical properties of two inks. The brown ink depicted in the bottom row appears homogeneous under UV illumination, but loses opacity under NIR light. The ink of the top row preserves more of its black color when the illumination is changed from VIS to NIR. XRF analysis demonstrated the presence of the iron-gall ink in both cases. In the left and right portions of Figure 9c, the distributions of the element iron extracted from the scans that crossed the lines drawn in the black ink of the main text and the brown ink of the comment were shown, respectively. In both cases, the amount of iron is much higher in the ink than in the paper as can be seen by the rise of its intensity when the scan reaches ink. Other elements whose profile matches that of the iron also belong to the ink. In the first case, these are potassium (K) and – very few - copper (Cu). In the second case, the ink of the comment, distribution of the elements potassium (K), manganese, (Mn), copper (Cu) and zinc (Zn) closely follow that of iron. Note that since the inks are different, two strikingly different sets of elements that comprise the inks were obtained. However, in both cases, inks contain elevated amount of iron and of the elements that are typical for iron-gall ink. Therefore, it was concluded that both texts were penned in different iron gall-inks (Figure 9d).

The paper shows intense foxing (browned spots), which indicates a high acid content in the paper (for example, lignin is found in especially high concentration in coniferous wood). Indeed, the pH value of the surface lay in the acidic range. The acid in the paper reacted with the acid in the iron-gall ink, leading to various signs of ink corrosion. Thus, the script has soaked through the paper, and around the script clear halos can be seen that show that the acid reaction has spread ever farther into the paper. The very short, slender fibers speak for a paper with wood content. The uniformly short fibres indicate that the paper pulp was beaten with a Hollander beater. The



**Figure 9a.** recto side with the documentation of the ink investigation (left); verso side of the fragment (right). Kitāb al-wathāiq, Abū Ishāq Ibrāhīm b. ‘Abd al-Rahmān al-Gharnātī (751/1350).

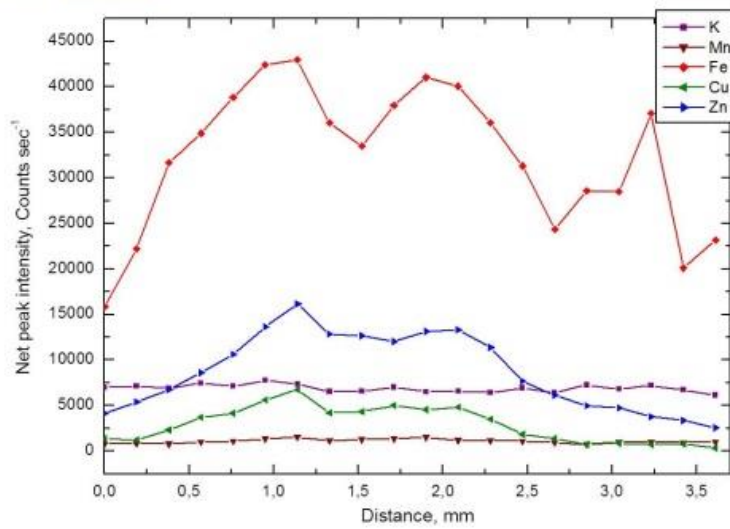
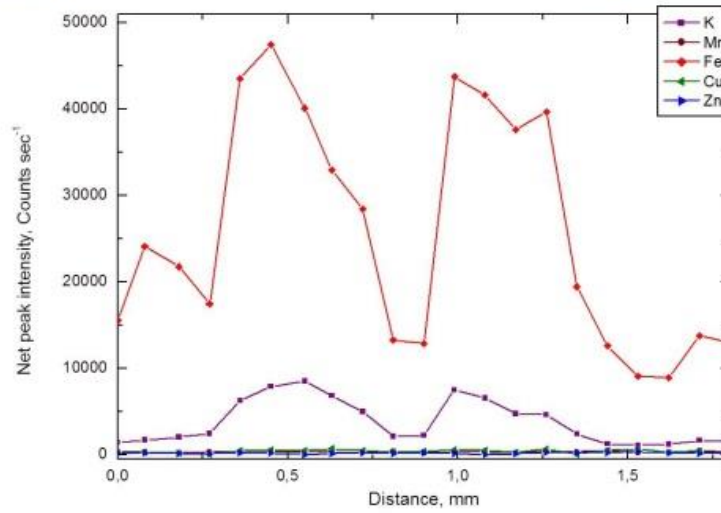


**Figure 9b.** Iron-gall ink of the comment (bottom row), iron gall ink of the main text (top row). The columns correspond to UV, VIS, and NIR illuminations, respectively.

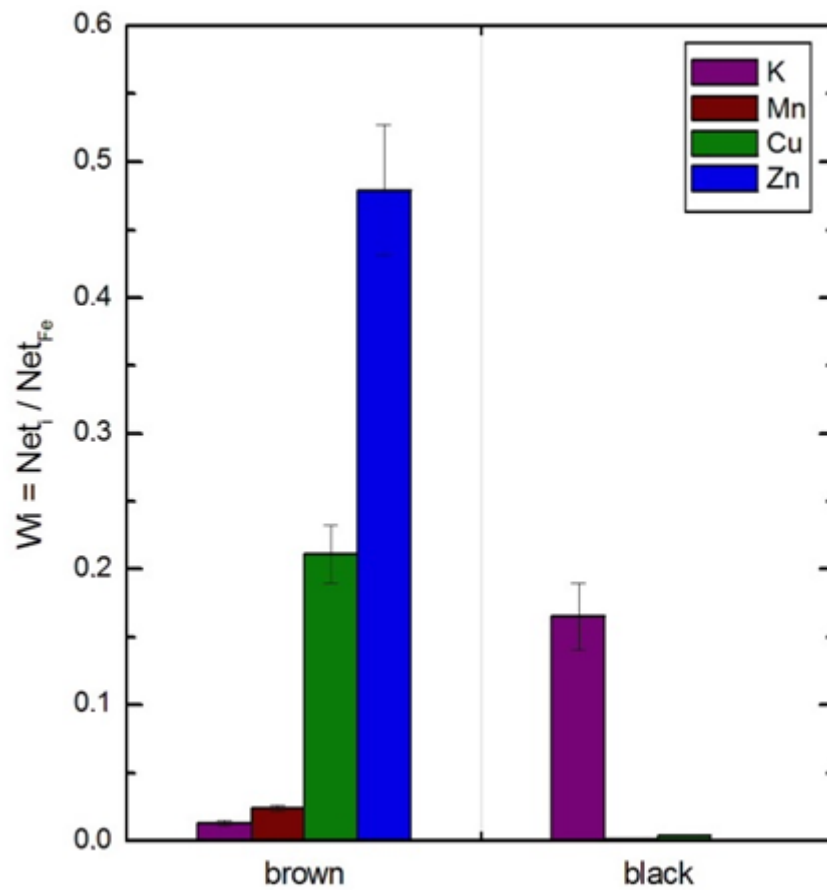
the paper pulp was beaten with a Hollander beater. The superficial and irregular ribbed structure probably did not result from the moulding process but was pressed into the paper afterward. The paper has no recognizable surface treatment like gluing or polishing, as is often found in Arabic paper (Figure 9e).

This manuscript page is unambiguously a European paper, industrially produced around 1900, because that is when wood-content paper first gained wide distribution. Acidic papers, in particular, were produced in times of scarcity or war, when the raw material wood was in short

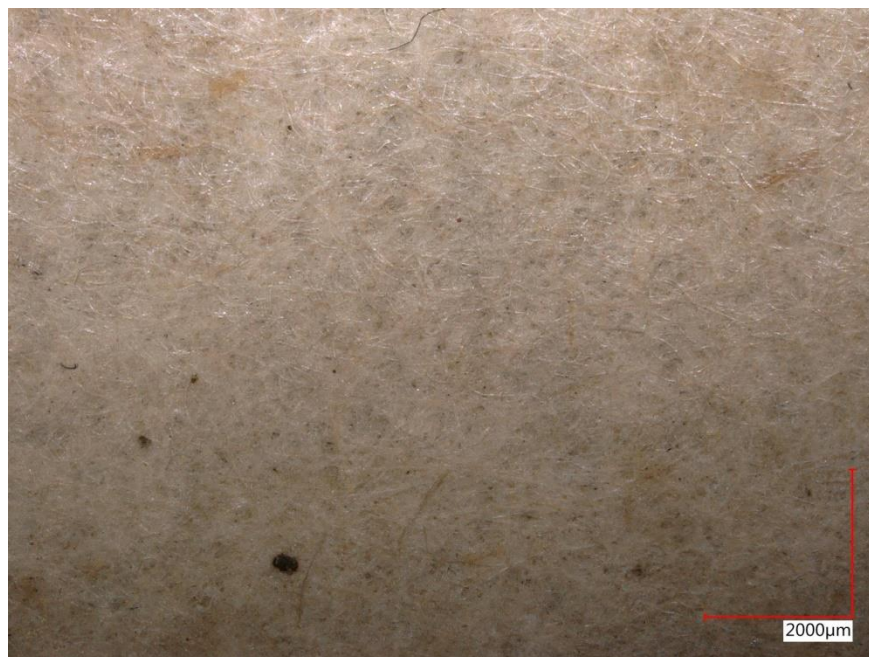




**Figure 9c.** Profile of the elements that follow iron in the ink of the main text (top) and of the comment (bottom).



**Figure 9d.** Fingerprint values (relative concentrations) of several elements in relation to iron.



**Figure 9e.** Non-treated paper surface.



Figure 10a. Recto (left) and verso side (right) of the fragment. Sharh ‘alā Alfiya Ibn Mālik (grammar).

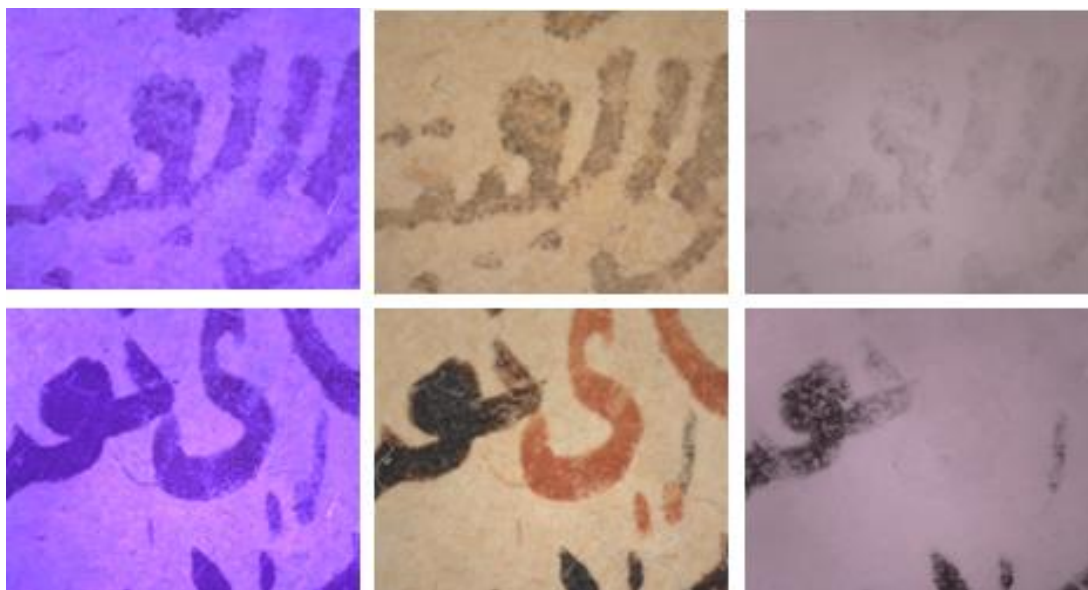


Figure 10b. Iron-gall ink of the comment (top row), mixed black ink and red ink in the main text (bottom row). The columns correspond to UV, VIS, and NIR illuminations, respectively.

supply and the lignin could not be adequately removed from the pulp. An even later dating, between 1914 and 1950, is even more probable.

**Sharh ‘alā Alfiya Ibn Mālik (grammar, Figures 10a-10d).** In contrast to the previous manuscript, here (Figure 10a) mixed carbon-iron-gall ink in the main text and comments executed in pure iron-gall ink were detected, with the onset of ink-induced corrosion. In this

manuscript, cinnabar-based red inks are also present. In this manuscript, however, the presence of both iron-gall and carbon ink can be recognized using reflectography alone (Figure 10b). In the ink of the comments the loss of opacity speaks for the identification of the type whereas in the ink of the main text high degree of un-mixing that occurred in the ink leads to the extensive loss of opacity in the borders of the letters when the text is viewed in the

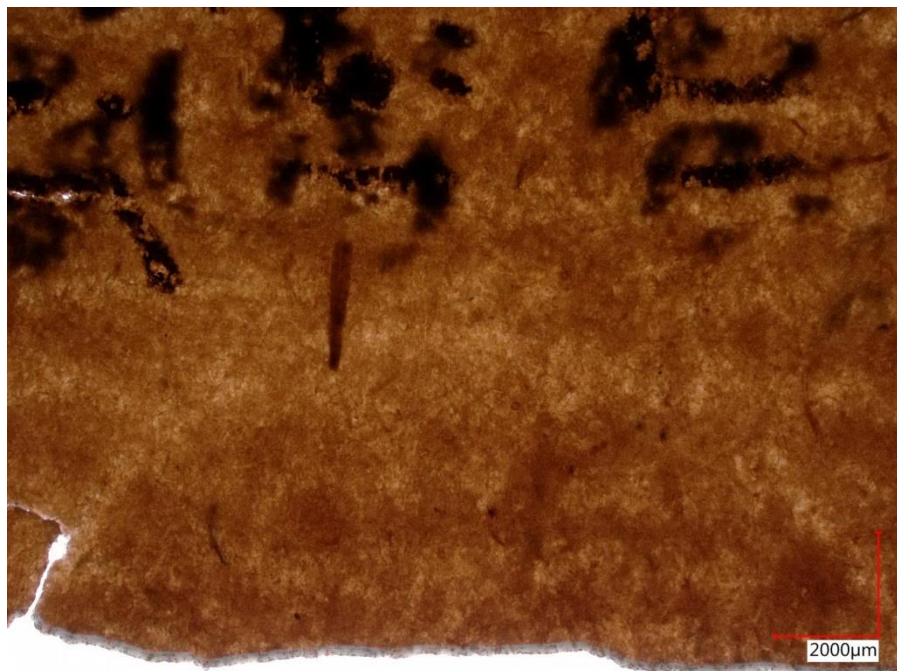


Figure 10c. Fragment of a watermark.

NIR light.

The paper displays traces of a watermark that unfortunately cannot be clearly recognized (Figure 10c) but allows us to identify this paper as a European one since Arabic papers have no watermarks. This was a 13<sup>th</sup> century Italian invention and was not used in the Arab world (Meggs, 1998). The paper contains shorter and longer fibers and the paper shows foxing overall. The paper substance is very unstable and brittle. All of the marginal areas of the paper have broken off. The unstable paper substance indicates that the fibers were treated roughly, which is typical of paper made in Europe from 1850 on. It seems that in this case, a mixture of rag fibers and ground wood was used, which would also attribute the paper production to the post 1850 period. Furthermore, when light is shone through the paper, a regular rib-and-web pattern is visible confirming the identification of the paper as European: it was customary in Europe to produce a hand-scooped paper using a metal sieve, into which a watermark was woven. Interestingly that in this case, it was coated with glue and polished, which treatment is not characteristic of Europe (Figure 10d). Much suggests that this manuscript page was handmade in Europe and only later given a glossy surface for the Arabic manuscript market, thereby making a European paper look Arabic, to conform to the taste of the later purchaser. The most probable dating is the 19<sup>th</sup> century.

**Kitāb Dalā'il al-khayrāt (prayers to the Prophet Muhammad PSL), Muhammad b. Suleymān al-Jazūlī (870/1465), Figures 11a-11c.** Here (Figure 11a), the text is written on European paper with short fibers. The

surface was treated with glue and polished. As with the previous manuscript, the paper can be placed in the 19<sup>th</sup> century. The decoration on the recto side contains carbon-based ink, gold, azurite, and red organic dye (probably cochineal, see Figure 11b). The text paragraphs on the verso side were written with two different iron-gall inks, both containing iron and potassium.

Here, most aspects of the paper's characteristics and dating correspond with the previous manuscript fragment. The paper substance is very unstable and brittle. Not only are all of the marginal areas of the paper broken off and in part repaired with a glued patch; a large flaw has also developed. In contrast with the previous manuscript (Sharh 'alā Alfiya Ibn Mālik) this fragment displays no watermark. The fibers are shorter, more regular (Figure 11c), and even less stable than those of the previous fragment, which speaks for the rougher treatment. This was taken as an indication that the paper was produced later, with the progress in industrialized papermaking.

**Kitāb fī al-Falak (astronomy) with Saharan writing, Figures 12a-12b.** Advanced ink corrosion indicates that the main text was executed in iron-gall ink, as revealed by the XRF analysis. Comments, too, were executed in iron-gall ink, though of a different composition (Figure 12b). In this manuscript, the red ink is not based on cinnabar as in previous manuscripts, but contains red lead.

The fragment displays no watermark. The dimensions of the paper show that it is only a half- or quarter-sheet. When light is shone through the paper, a regular rib-and-web pattern is visible. The fibres are long and irregular, suggesting high-quality rag fibre. It was probably made

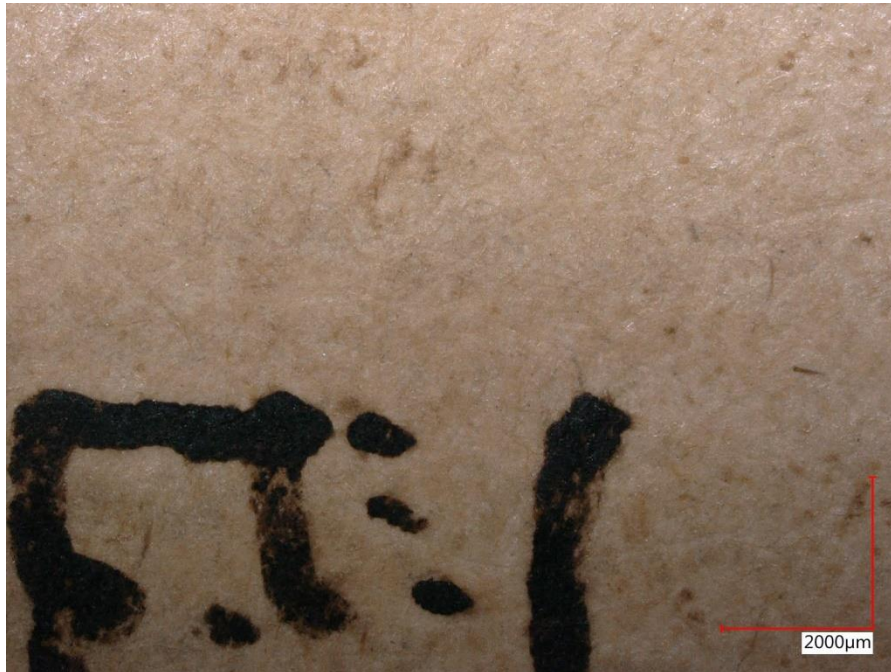


Figure 10d. Treated surface.



Figure 11a. Recto (left) and verso side (right) of the fragment. Kitāb Dalā'il al-khayrāt (prayers to the Prophet Muhammad PSL), Muhammad b. Suleymān al-Jazūlī (870/1465).

before 1850, when more rag fibre was used. The paper substance is stable and not very brittle. The fibres were not treated as roughly as in the previous fragments (Sharh 'alā Alfiya Ibn Mālik, Figure 10a and Kitāb Dalā'il

al-khayrāt, Figure 11a), suggesting a somewhat earlier production date. Furthermore, the paper surface experienced intense post-production treatment. The surface is high-gloss and polished, which would be

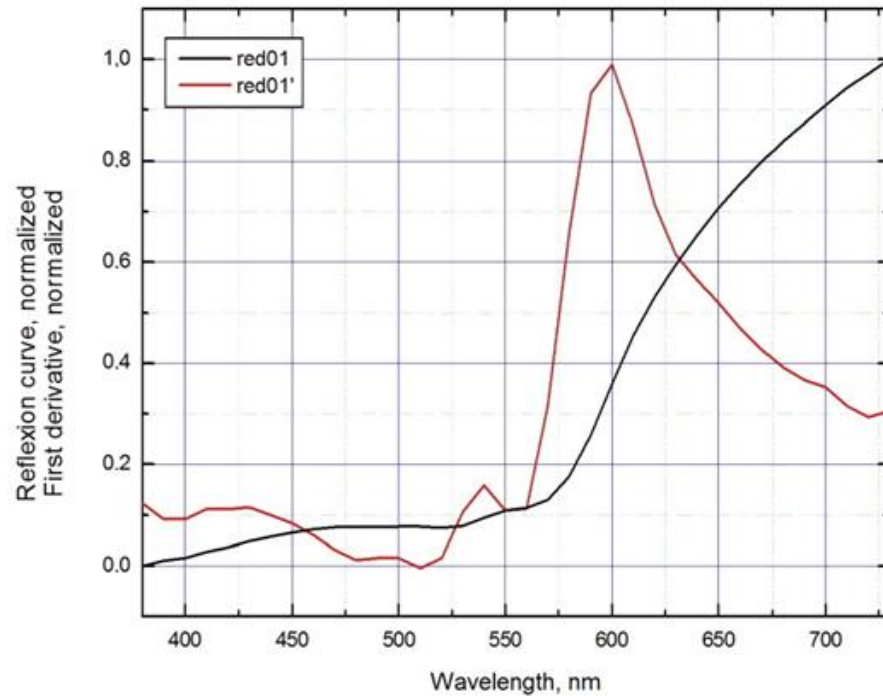


Figure 11b. VIS-spectrum revealing a red organic dye (cochineal).

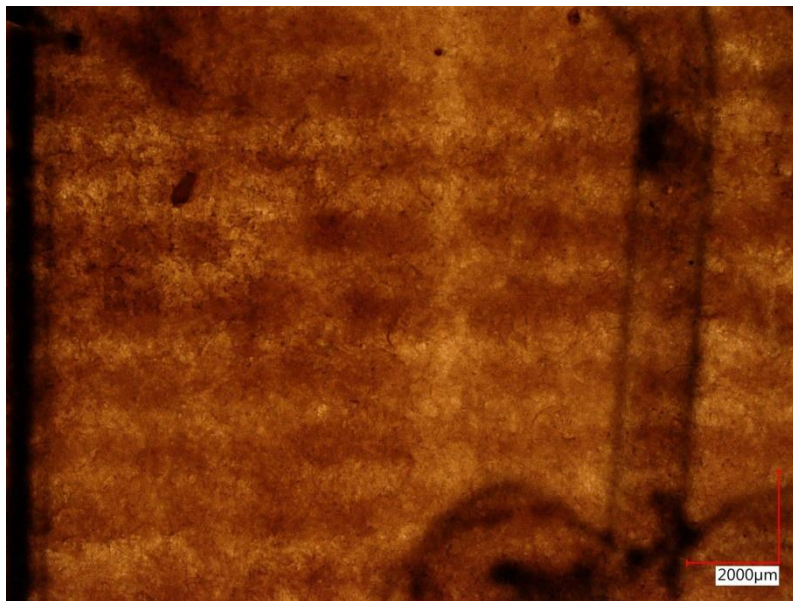


Figure 11c. Transmissive light revealing the paper structure.

unusual for European paper.

**Kitāb fī al-Hadīth (tradition of the Prophet Muhammad PSL) with Oriental writing, Figures 13a-13d.** The text was written with black and brown iron-gallinks (Figure 13b). The red ink is based on cinnabar. The paper has a cloudy structure (Figure 13c). The fibers

are long and very irregular. Long, dark fibers can be clearly seen, distributed throughout the whole paper. This paper has a marked rib structure, but no webbing is visible. The broad ribs and the lack of webbing indicate a non-European paper. This could be Indian or Arabic paper. The surface is glossy and has a coating (Figure 13d).



**Figure 12a.** Recto (left) and verso side (right) of the fragment. *Kitāb fī al-Falak* (astronomy) with Saharan writing.

The surface sizing of the coating clearly displays a brushstroke structure. This technique is typical for an Arabic paper. The most probable dating is before 1900; it is quite possible that the paper is much older.

**Īthār al-Insāf fī al-Akhlāq (ethics), Abū Muzfar Yūsuf Sibṭ al-Māridīnī (Sibṭ ibn al-Jawzī) (654/1257). Figures 14a-14c.** In this manuscript, two types of paper glued together were found, making close inspection and classification impossible. It is seen though that both sides were polished but only one side was treated with glue (Figure 14b). The texts are executed in carbon and iron-gall inks as well as gold and red different cinnabar inks (Figure 14c). Presence of different trace elements in the red inks indicates tentatively that mineral cinnabar was used as a precursor for the inks (Nöller, 2012).

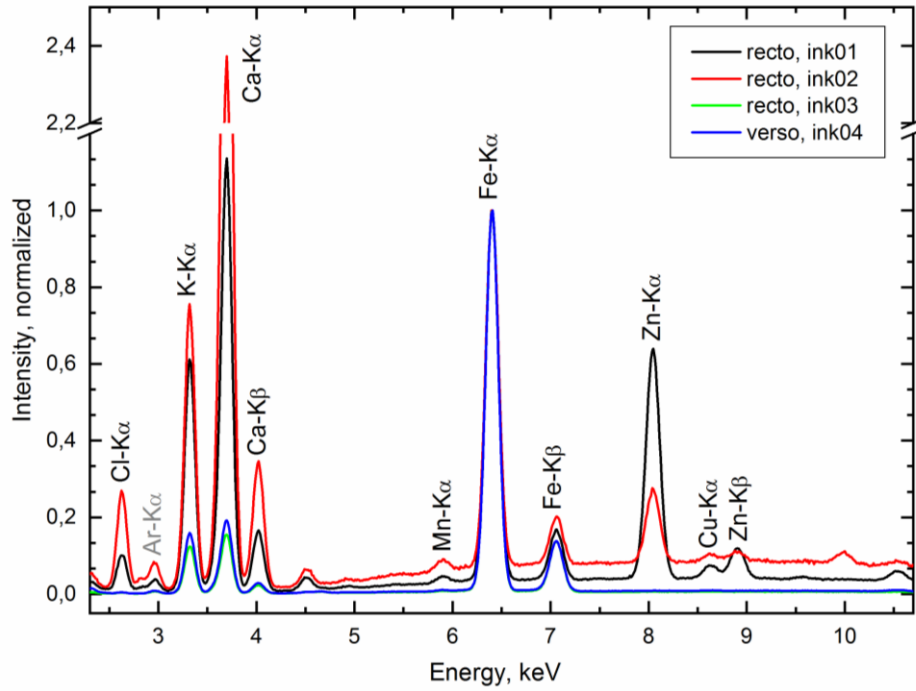
**Al-Hulal al-Sundussiyat fil Maqāmāt al-Ahmediyyat al-Qudussiyat (literature), Ahmad b. ʿAbd al-Hayy al-Halabī (1120/1708). Figures 15a-15c.** The texts were written with various iron-gall inks that contain different relative concentrations of copper and zinc (Figure 15b). In addition, decorations were executed with a carbon-based ink, gold, and azurite. It was impossible to identify the yellowish dye.

The paper displays no watermark, but one could have been cut off. The dimensions of the paper show that it is only a half- or quarter-sheet. When light is shone through the paper, a regular rib-and-web pattern is visible. The fibers are long and irregular, suggesting high-quality rag fiber. The paper substance is stable and not very brittle. The paper substance is comparable to that of the fragment from *Kitāb fī al-Falak* (Figure 12a), but here it is

in better condition and shows no foxing. The coating is unusual for European paper. The surface is high-gloss and polished (Figure 15c). The foxing of the paper and the ink corrosion on its surface could be a result of this sizing. Resin sizings also contain acid. Customary with handmade papers in Europe was a light, animal-based surface sizing. Polished surfaces are rare in papers, more common in parchments. The research used rags and was hand-scooped with a metal sieve. It was probably made before 1850, when more rag fiber was used. It was produced in Europe and only afterward given a glossy surface to make a European paper look Arabic for the Arabic manuscript market and to meet the taste of the later purchaser. The most probable dating was the 18<sup>th</sup> to 19<sup>th</sup> century.

**Quran with decorated and gilded Maghrebinian writing, Figures 16a-16c.** The main text was written with a carbon ink. Additional texts and decorations were executed in gold ink, blue azurite, and an organic red dye, probably cochineal (Figure 16b). Most aspects of the characteristics and dating of the paper correspond with those of the manuscript *Kitāb Dalā'il al-khayrāt* (Figure 11a), that is, European paper with short fibres (Figure 16c).

The paper substance is very unstable and extremely brittle. The marginal areas have broken off. There is a truncated watermark. The fibres are short, regular, and unstable, which speaks for a rough treatment of the fibres, which can indicate that the paper was made later, with the progress of industrialized papermaking. The most probable dating is therefore the 19<sup>th</sup> century.



**Figure 12b:** Characteristic XRF-spectra of different inks from fragment 4. For better comparability the Fe-K $\alpha$  peaks were normalized to 1.



Recto side



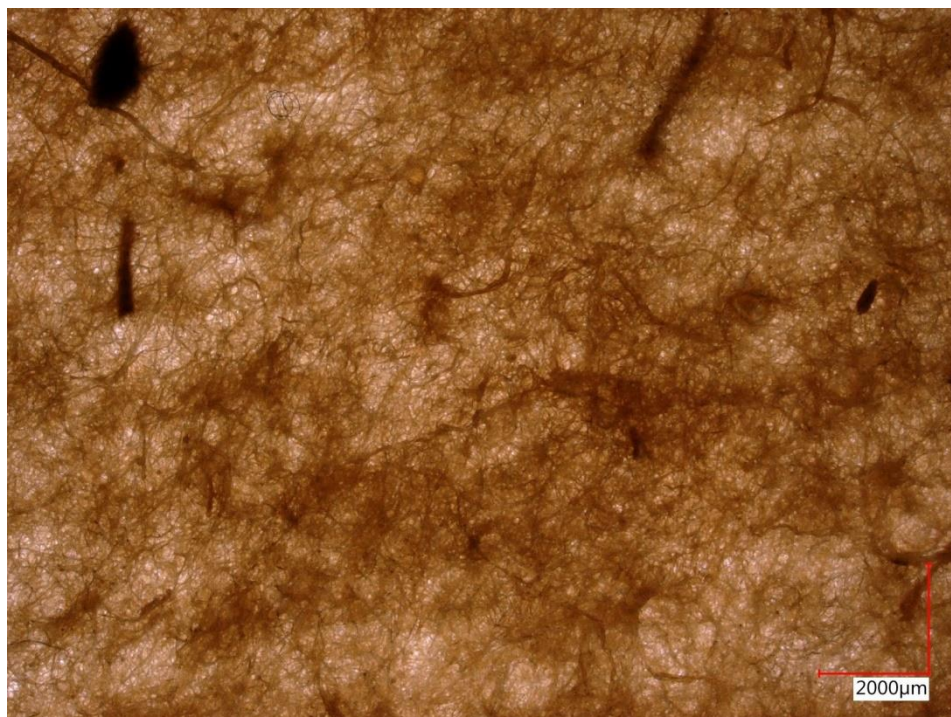
Verso side

**Figure 13a.** Recto and verso side of the fragment. Kitāb fī al-Hadīth (tradition of the Prophet Muhammad PSL) with Oriental writing.





**Figure 13b.** Iron-gall ink of the comment (top row), iron-gall ink of the title (bottom row). The columns correspond to UV, VIS, and NIR illuminations, respectively.



**Figure 13c.** Transmissive light reveals the paper structure

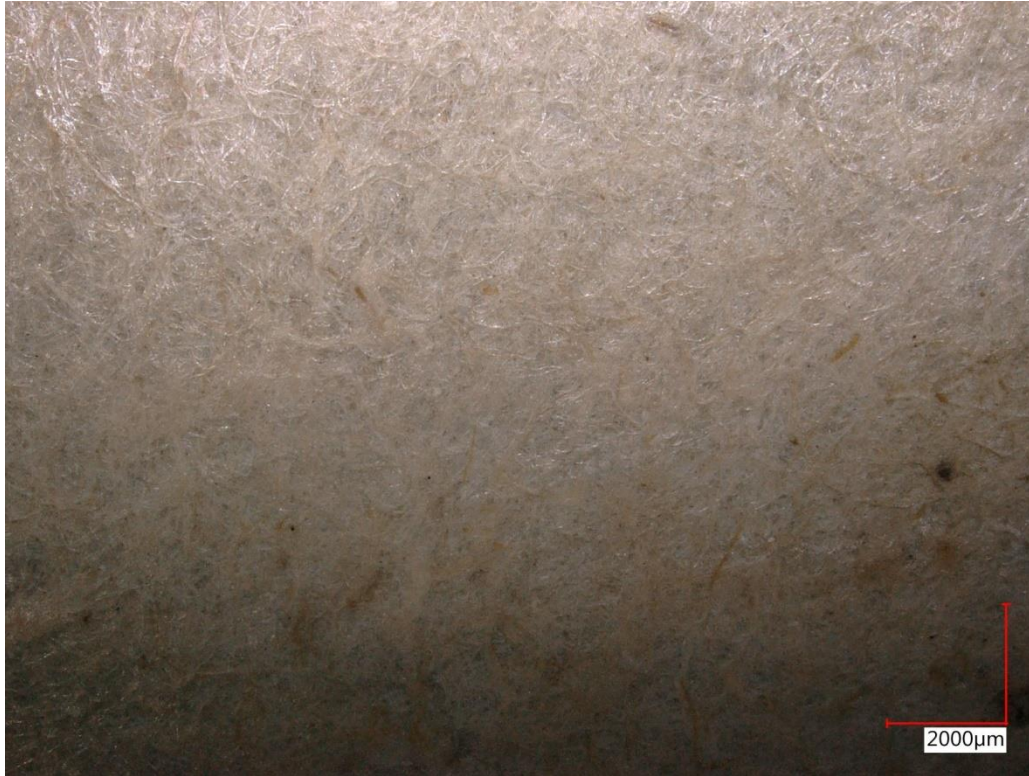


Figure 13d. Treated paper surface.



Figure 14a. Recto (left) and verso side (right) of the fragment. *Īthār al-Insāf fī al-Akhlāq* (ethics), Abū Muzfar Yūsuf Sibṭ al-Māridīnī (Sibṭ ibn al-Jawzī) (654/1257), with Oriental and gold writing.



Figure 14b. Treated paper surface.

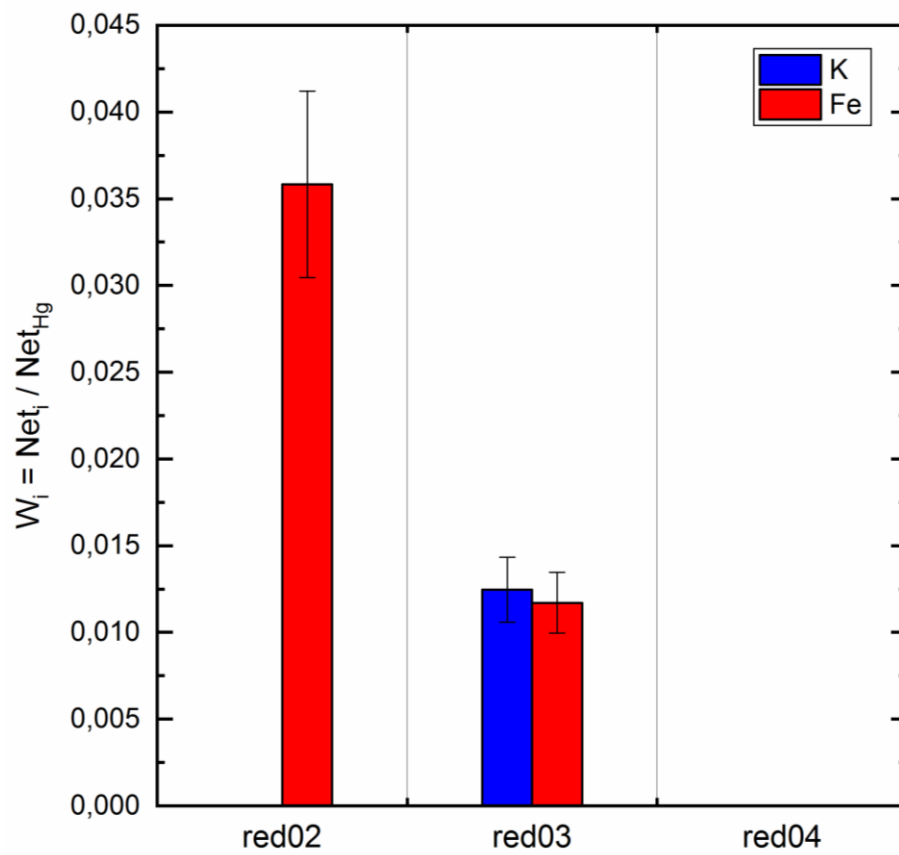
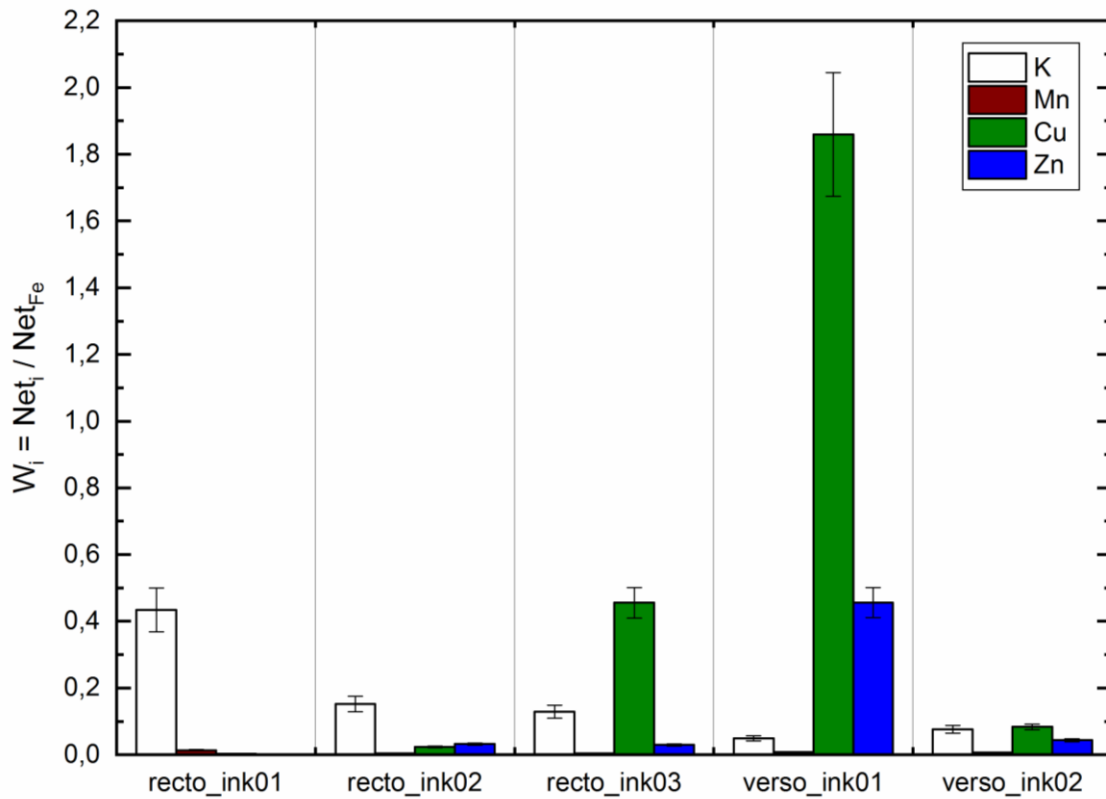


Figure 14c. Fingerprint values of several trace elements in relation to mercury.



**Figure 15a.** Recto (left) and verso side (right) of the fragment. *Al-Hulal al-Sundussiyyat fil Maqāmāt al-Ahmadiyyat al-Qudussiyyat* (literature), Ahmad b. ‘Abd al-Hayy al-Halabī (1120/1708), with Maghrebinian and gold writing.



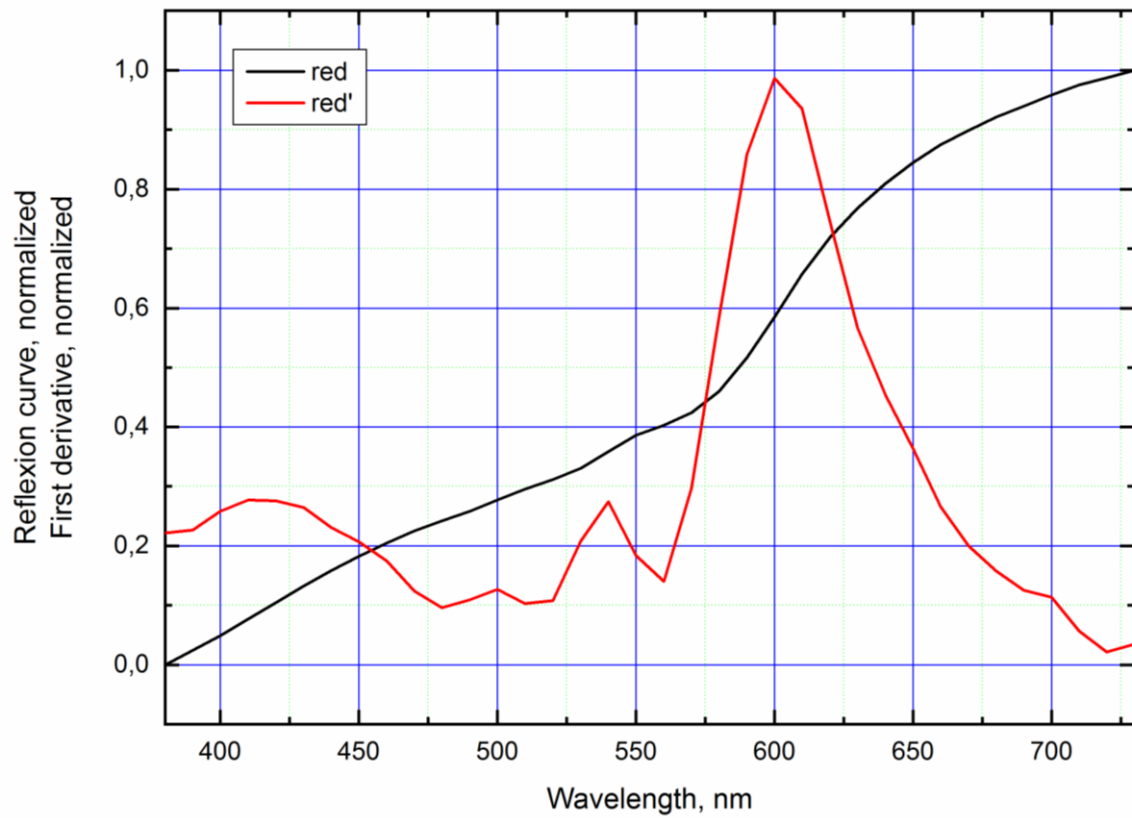
**Figure 15b.** Fingerprint values (relative concentrations) of several elements in relation to iron.



Figure 15c. Treated paper surface.



Figure 16a. Recto (left) and verso side (right) of the fragment from Quran with decorated and gilded Maghrebinian writing.



**Figure 16b.** VIS-spectrum revealing a red organic dye (cochineal).



**Figure 16c.** Transmissive light reveals the paper structure.

## CONCLUSION

The results of the analyses of the reference materials indicate that one can recognize the local materials if they are used in the real manuscripts. In addition, it is possible not only to classify writing inks (typology) but also to differentiate between the different inks of the same type (fingerprinting). Meanwhile the research created a first structured collection of traditional recipes for producing black and coloured inks in Mali. The reference database will be expanded to include more materials and analyses to produce a solid base for comparison with original manuscripts. However, already at this stage one could begin with the analytic work on the original manuscripts in Bamako. For future analysis, the manuscripts will be sorted according to the type of inks (pigment inks, dye inks, etc.), to the type of applicable analyses and to the kind of sampling allowed by the libraries that own the manuscripts. These case studies show the maximum output of information that can be extracted with non-destructive methods. Though different paper types were found, no paper type could be ascribed with certainty to Malian production. In addition, several inks, dyes, and pigments were characterized in the pilot samples. The presence of different papers, inks, and colorants suggests different production sites and techniques.

Although practically all the types of the paper tested here were identified as European, they have clearly been subjected to a treatment that made them look like Arabic paper. It is believed that this was a common practice to make the paper look more attractive for the Arab market.

The results of the above case studies should encourage philologists and conservators working with manuscripts to enlist support from experts in material analysis. The most important precondition for these results is the formulation of precise research questions or hypotheses. More generally, the authors hope that material analysis will soon become an integral part of the emerging field of manuscriptology, uniting philology, codicology, and palaeography, as well as conservation science.

## CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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