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# Assessment of a multi-technical non-invasive approach for the typology of inks, dyes and pigments in two 19th century's ancient manuscripts of Morocco

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ABSTRACT

A rich and non-invasive multi-technique study has been carried out on two ancient Moroccan manuscripts, dealing with theology, written in the 19th century and belonging to different scribal schools of the western Arabic Mediterranean region. Currently, Moroccan manuscripts investigations are limited to codicological studies in which reports on illuminations and colored vocalizations are limited to visual descriptions. Hence scientific investigations are required for an objective characterization of this universal heritage. The integration of elemental and molecular information acquired by μ-XRF, μ-XRD, μ-Raman, μ-SERS, reflection mid-FTIR, UV–vis reflectance and UV–vis fluorescence has allowed for the characterization of both inorganic pigments and organic dyes. The inorganic pigments have been identified and characterized by combining the elemental XRF information with molecular infrared and Raman investigations. XRD analyses have been also carried out for the identification of crystalline compounds. Vermillion, orpiment, azurite, lead chromate, emerald green, Scheele's green and artificial ultramarine were identified. Red and yellow organic dyes have been identified by combining SERS, UV–vis reflection and UV–vis fluorescence spectroscopic techniques. The signals detected on red colors were assigned to the animal carminic anthraquinone, while those detected on yellows seem originating from a natural flavonoid. The present study, which is the first complete one undertaken on ancient Islamic documents of Morocco and being extended in situ to other artworks, unique in the Arabic world and available at the Moroccan libraries, will contribute to promoting codicological investigations, dating and authenticating some manuscripts and giving elements of response, useful for art history, in the knowledge of coloring materials used in the western Mediterranean Arabic region during the 19th century.


## 1. Introduction

Despite the great importance of the Moroccan documentary heritage dealing with Quran, theology, mathematics, astrology, medicine, history, pharmacy, Arabic literature and other topics, only limited codicological studies have been carried on this universal heritage. Each manuscript constitutes a unique artwork handcrafted in a personalized manner as the artists were used to innovate and maintain secret their personal touches. Excluding the single, on site, work undertaken by Roger on some manuscripts of the National Library of Rabat [1], no scientific investigation was devoted to the art crafts of the time; ancient coloring materials were described only by visual observation, then subjectively, and no objective data are available neither for art history nor for confirming advanced creation periods of artworks. During the recent years there has been an increasing interest in the use of non-invasive analytical techniques able to yield valuable information on ancient pictorial art by non-contact examination of entire artworks surfaces. Pigments and dyes are considered as technological/chronological markers; their identification is considered as a potential technical approach to discriminate between original and fake artworks [2].

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In this sense, the present work is the continuation of our recent study [3] which constitutes the first scientific qualitative and multi-technical analysis of inks and coloring materials in ancient Moroccan manuscripts.

Two manuscripts dealing with theology, attributed to the 1800s and belonging to two completely different scribal schools, are studied by a multi-technical and non-invasive analysis combining elemental and structural techniques. The goals are to confirm the advanced dating of the two manuscripts and to enrich the knowledge of the pictorial materials used in the western Arabic Mediterranean region during the 19th century.

The non-invasive μ-Raman, μ-SERS, μ-XRF, μ-XRD, Mid-FTIR, Fiber Optical Reflectance/Fluorescence spectroscopies are the techniques used.

## 2. Experimental

### 2.1. Manuscripts description

The artworks are shown in Fig. 1a. Both manuscripts are familial heritages belonging to private persons from the imperial cities of Meknes and Fez.

Manuscript MEK-MS-7 is a, 12 cm × 11 cm, 19th century's copy of the famous "Dala'il al-Khayrat" consisting of a collection of prayers in addition to a description of "Arrawda Acharifa" shown in MEK-MS-7-$P_3$ (burial ground of the Prophet Mohammed and his two successors Abou Bakr and Omar); the scribe/copyist of the manuscript MEK-MS-7 died in 1869. The original work was written during the 15th century by the Moroccan Sufi Muhammad Al-Jazuli. In Fig. 1a, the pages under study are presented.

Manuscript MEK-MS-8 is a, 2.5 cm × 17.2 cm, 19th century's theology report. The author was the Moroccan theologian Mohammed Taoudi Bensouda, died at the end of the 18th century. The scribe died in 1926; the whole of his handcrafted works date back to the 19th century. It is believed that the manuscript MEK-MS-8 dates also back to the 19th century. The artifact shows a single decorating panel at the top of the first page MEK-MS-8-$P_1$.

The chromatic measurements recorded on both manuscripts, reported in Fig. 1b, present a large palette of colors in addition to the black used for the bulk of writings.

### 2.2. Equipments and methods

In order to respect the integrity of the artworks, no sampling was done; measurements were performed only by contact at a distance of about less than 1 mm to 2 cm.

#### 2.2.1. Colorimetric measurements

A portable Konica Minolta CM700d spectrophotometer working in the range 400–700 nm, with a D65 illuminant was used. Average values were obtained from at least five measurements.

#### 2.2.2. Micro X-ray fluorescence measurements

The portable set up is that one already described in ref. [4]; it is made up of an X-ray generator (EIS s.r.l. P/N 9910), equipped with a tungsten filament, and a Peltier cooled silicon drift detector (SDD) with a resolution of about 150 eV FHWM at 5.9 keV. The system working in non-contact mode was generally positioned at a distance of about 2 cm from the point of interest. The detectable elements are those with atomic number $Z \geq 14$. In all the experiments, the source was operated at 38 kV and 0.01 mA; so the detected energy ranges between 0 and 30 keV. Data acquisition time was 120 s. The geometrical set-up was normal beam incidence, 4 mm beam diameter (and achievable spatial resolution), and 45° take-off angle of the emitted radiation.

#### 2.2.3. Raman measurements

Micro Raman spectra were carried out using a Renishaw RM 1000 spectrometer equipped with a CCD detector and an external Leica DMLM confocal microscope with 5×, 20×, 50× and 100× objectives. The excitation source is a He–Ne laser operating at 632.8 nm with a resolution better than 2 $cm^{-1}$. The laser beam was focused, directly on the manuscript sheet without any sampling, using either 50× or 100× objectives; the spectra were recorded as extended scans and acquisition times were adopted in the range 1–5 s. In order to safeguard the integrity of the artwork, the laser power at sample was held as low as possible; the adopted powers ranged between 0.2 and 1.9 mW.

SERS analysis was accomplished by using hydroxylamine Ag nanoparticles prepared by reduction with hydroxylamine as reported in ref. [5]. A total of 300 mL of a sodium hydroxide solution (1 M) was added to 90 mL of a $6 \times 10^{-2}$ M hydroxylamine hydrochloride solution. Then, 10 mL of a $1.11 \times 10^{-3}$ M silver nitrate aqueous solution was added drop wise to the mixture under vigorous stirring. The resulting suspension had an extinction maximum at 410 nm, corresponding to spherical nanoparticles with an average diameter of 45 nm [5]. Without any previous aggregation or pre-concentration of Ag nanoparticles, an aliquot of the Ag colloid (1 mL) was deposited on the selected area of the manuscript, thus leading to a very small and imperceptible spot. Then, SERS measurements were collected after drying the deposited area.

The identification of the coloring pigments was achieved by comparison with Raman spectral libraries [6,7].

#### 2.2.4. Mid-FTIR IR measurements

Reflection mid-FTIR spectra were carried out, as already described in ref. [8], with a portable infrared spectrophotometer ALPHA-R Bruker Optics equipped with a Globar Mid-IR source, a modified Michelson interferometer to work in all spatial conditions (RockSolidTM) and a room-temperature DLaTGS detector. Sampling was carried out by an external reflectance module with specular optics (22°/22°); the sampled spot had a diameter of about 6 mm. A total of 200 interferograms were acquired in the spectral range 7500–375 $cm^{-1}$ with a spectral resolution of 4 $cm^{-1}$. The reflectance profile ($R$) is expressed as pseudo-absorbance, $\log(1/R)$.

#### 2.2.5. Micro X-ray diffraction measurements

μ-X-ray diffraction spectra were measured as already described in ref. [9]; they were collected with a PANalytical X'Pert PRO diffractometer equipped with a conventional X-ray tube (Co Kα radiation, 40 kV, 30 mA, line focus) and a multi-channel detector X'Celerator with an antiscatter shield. The measurements were performed in the range from 10 to 100° ($2\theta$) with step of 0.0334° and 160 s counting per step. In this case, we used the conventional Bragg–Brentano geometry with 0.04 rad Soller slit, 0.5° divergence slit, 1° anti-scatter slit and 15-mm mask in the incident beam; and 5.5-mm anti-scatter slit, 0.04 rad Soller slit and Fe beta-filter in the diffracted beam. XRD patterns were not pre-treated before interpretation, as no background correction was needed.

#### 2.2.6. UV–vis reflectance and fluorescence

UV–vis. measurements were performed as described in ref. [10]. Reflectance measurements were undertaken using a portable spectrophotometer composed of Avantes parts and a deuterium halogen lamp (AvaLight-DH-2000-FHS) as excitation source. An integrating sphere with a 6 mm diameter viewing aperture (ISP-30-6) is used to collect and transfer the reflectance signals to a AvaSpec-2048 CCD detector via quartz fiber optic system (diameter 600 mm). The AvaSoft software controls the acquisition of the spectra in the 200–1100 nm range. The spectral resolution is about 1.4 nm. Fluorescence spectra were collected using a portable fluorimeter, assembled as a prototype from individual components