Colorimetric and spectral reflectance access to some ancient Egyptian pigments

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In ancient Egypt, colour expressed both symbolic and aesthetic value. In the present study, a colorimetric spectral reflectance analysis of some ancient pigments from the mortuary temple of Medinet Habu, Luxor, Egypt (1184-1153 BC) is reported. Six groups of pigments were selected for analysis as follows: blue, green, yellow, red, brown and black. The chromatic coordinates and the reflectance spectra were recorded in the visible light range (400-700 nm) via a portable reflectance spectrophotometer. Additionally, microscopic observations on the samples and morphological-microanalysis were performed. The analyses conducted on the studied pigments have provided significant information on their composition and hues. The results emphasized the value of the spectral reflectance analysis as a helpful tool to study pigments in polychromatic surfaces.

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Introduction

Colour is an important feature of a pigment material. In fact, colour is relevant to the characterization of a spectral property resulting from the diversion of luminous radiation when it interacts with a matter [1]. For an object, the relative reflectance at different wavelengths define its reflectance spectrum \( R(\lambda) \), which could also be defined as a fingerprint of each pigment [2]. Because of the significant information they provide, the visible reflectance spectra and the colorimetric coordinates are essential measurements for restoration procedures of cultural heritage materials [3].
Colour measurements help to documenting the chromatic palette used in certain objects and to observe any chromatic alterations. Routinely, several analytical methods have been dedicated to identify ancient pigments. Vibrational and spectroscopic techniques enable direct and fast identification of the contained minerals over tiny samples. Raman microscopy is a sensitive non-destructive tool has been used successfully to characterise individual grains in pigment samples [4-5]. Additionally, the scanning electron microscopy showed extensive advantages in characterizing painted objects. Using scanning electron microscope, the morphological-microstructure features of pigment and microchemical analysis could be determined [6]. Regarding colour measurements, numerous studies have been undertaken to report the importance of the colour measurements in the field of cultural heritage preservation. Colorimetry was used successfully to document different art works of graphic documents, oil paintings, wall paintings and stone structures [7]. Marchiafava et al. [8] have reported that colour measurements were helpful in monitoring the conservation process applied to the mural Tuttomondo (1989) painted by Keith Haring (1958-1990) on the wall of the Church of Sant’Antonio Abate in Pisa (Italy). The comparison of the colorimetric data of fabricated black pigments and black pigment from the Roman age (from the Augustus small study room, Palatino, Rome-30 BC) revealed that the ancient pigment was probably a black vine pigment [9]. Further, colorimetry was used as a beneficial tool to follow the fading of the red-orange realgar pigment (α-As4S4) on ancient Egyptian Papyri [10]. To record the reflectance spectra of a material, devices such as spectrophotometers and tristimulus colorimeters allow numeric expression values of samples. A spectrophotometer illuminates the sample with monochromatic or polychromatic light in the visible spectrum (between 400 and 700 nm), then, it measures the reflection (or transmission) values [11].

The CIE (Commission Internationale de l’Eclairage) 1976 (L*a*b’), or the CIELAB system, is widely used for recording the chromatic coordinates. This system, referred to as colorimetry, is far superior and works as an effective tool for visualizing the colour [12]. Likewise, it allows a quantitative registration of the chromatic variations in the composition of the bulk material [13]. Three coordinates of this system are represented in the form of the lightness L’, ranging from 0% to 100%. The hue coordinate a’ corresponds for the green (negative) to red (positive), while the hue value b’ is for the blue (negative) to yellow (positive). Based on the differences in the reflectance spectrum, which is typical of each pigment, the particular behaviour of a painted surface could be identified [14]. Having said that several potential factors may affect the colour measurement, for instance degradation processes on the pictorial surface, moisture content of materials, surface roughness and particle size [15].

**Pigments**

According to Color Pigments Manufacturers Association, “pigments are colored or fluorescent particulate organic or inorganic solids which usually are insoluble in, and essentially physically and chemically unaffected by, the vehicle or substrate in which they are incorporated”. Pigments are derived from a broad of sources and could be classified according to their colour and chemical composition [16]. To give an illustration, common inorganic colouring substances are of oxides, sulphides, carbonates, sulphates, phosphates and silicates of the heavy metals. The chromatic characteristics of materials are highly affected by size, shape and texture of pigment grains. In comparison to earth pigments, the coarse grains of the Egyptian blue pigment come out of poor hiding power [17]. The particle size classification for pigments is given in Table 1 [18].
### Table 1: Particle size classification for pigments (Feller and Bayard, 1986).

<table>
<thead>
<tr>
<th>Absolute particle size</th>
<th>Relative particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 40μm</td>
<td>Very coarse</td>
</tr>
<tr>
<td>10–40μm</td>
<td>Coarse</td>
</tr>
<tr>
<td>10–3μm</td>
<td>Large</td>
</tr>
<tr>
<td>3–1μm</td>
<td>Medium</td>
</tr>
<tr>
<td>1.0–0.3μm</td>
<td>Fine</td>
</tr>
<tr>
<td>&lt; 0.3μm</td>
<td>Very fine</td>
</tr>
</tbody>
</table>

**Case study**

The memorial temple of Medinet Habu is located in the west bank of Luxor, Upper Egypt. The temple was built on the order of the Pharaoh Ramses III (1184-1153 BC) [19]. The stone walls of the first and second court of the temple are coloured with multiple chromatic palette. The scenes of the temple were carved in the form of sunken inscription and sunken-raised reliefs.

**Research aim**

For the purpose of cultural heritage preservation, collecting data on materials and ancient technology is an important issue. The present study emphasises the importance of registering chromatic values and visible reflectance spectra on ancient polychromatic surfaces. Analysing the spectral reflectance can be used to provide valuable information on the pigment materials.

**Analytical methods**

**Spectral reflectance analysis**

The reflectance spectra were recorded on the studied samples through a HunterLab Miniscan® XE Plus spectrophotometer. The chromatic values were expressed as colour coordinates in the CIE $L^*a^*b^*$. This colour system enables the determination of hue and lightness intensity of samples. The operating conditions of the apparatus were:

- Illuminant D65/10° Observer
- Spectral Range: 400-700 nm; spectral Resolution: 10nm
- Choice of viewed sample area: 25mm (1.00 in)

The spectrophotometer was provided with its own white reference (100% reflective) and a zero calibration box (0% reference). The data reported were as an average of three measurements with a measuring aperture of 8 mm. Then the data were calculated for the CIE $L^*a^*b^* 1976$ colour space. Studying of the recorded spectra was performed via online database and literature data in the field. Actually, no sample’s preparation was made for measurements, only the dust layers on the pictorial surfaces were removed using a soft brush.

**Visual observations**

An Olympus SZ-40 stereomicroscope was used to examine the pigment grains and the digital shots have been captured with an Olympus DP10 digital camera.
Morphological-microchemical analysis

Morphological-microstructural photomicrographs were obtained on the samples through an environmental scanning microscope (model Philips XL-30 ESEM) equipped with an X-ray microanalysis spectrometer (EDAX, Apollo SDD 10). Unlike the conventional scanning electron microscope, the environmental scanning electron microscope enables a non-conductive investigation on samples. However, polished cross-sections on the pictorial layers can be coated with a carbon or metallic layer. Regrettably, this is a destructive procedure to the archaeological samples.

Results and discussion

The CIE $L^*a^*b^*$ values recorded on the studied pigment samples are given in Table 2 and Figure 1. Table 3 demonstrates the EDAX elemental analysis (%) obtained on the studied samples.

<table>
<thead>
<tr>
<th></th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue I</td>
<td>45.7265</td>
<td>-13.765</td>
<td>-17.432</td>
</tr>
<tr>
<td>Blue II</td>
<td>46.3254</td>
<td>-12.652</td>
<td>-16.432</td>
</tr>
<tr>
<td>Blue III</td>
<td>44.3654</td>
<td>-11.432</td>
<td>-17.432</td>
</tr>
<tr>
<td>Green I</td>
<td>65.0987</td>
<td>-14.325</td>
<td>2.342</td>
</tr>
<tr>
<td>Green II</td>
<td>65.8907</td>
<td>-9.6757</td>
<td>3.655</td>
</tr>
<tr>
<td>Green III</td>
<td>64.354</td>
<td>-10.765</td>
<td>1.4382</td>
</tr>
<tr>
<td>Yellow I</td>
<td>74.8395</td>
<td>5.9987</td>
<td>27.765</td>
</tr>
<tr>
<td>Yellow II</td>
<td>72.3457</td>
<td>5.4355</td>
<td>26.324</td>
</tr>
<tr>
<td>Yellow III</td>
<td>66.6547</td>
<td>7.5118</td>
<td>23.5238</td>
</tr>
<tr>
<td>Red I</td>
<td>50.4327</td>
<td>35.5543</td>
<td>23.4232</td>
</tr>
<tr>
<td>Red II</td>
<td>48.6543</td>
<td>35.5245</td>
<td>21.3455</td>
</tr>
<tr>
<td>Red III</td>
<td>50.6547</td>
<td>36.2456</td>
<td>22.1246</td>
</tr>
<tr>
<td>Brown I</td>
<td>34.1453</td>
<td>29.7741</td>
<td>13.5031</td>
</tr>
<tr>
<td>Brown II</td>
<td>33.8464</td>
<td>21.0177</td>
<td>13.5855</td>
</tr>
<tr>
<td>Brown III</td>
<td>34.0609</td>
<td>20.5678</td>
<td>12.9639</td>
</tr>
<tr>
<td>Black I</td>
<td>22.5491</td>
<td>-0.1167</td>
<td>-0.0735</td>
</tr>
<tr>
<td>Black II</td>
<td>22.6241</td>
<td>-0.0837</td>
<td>-0.0317</td>
</tr>
<tr>
<td>Black III</td>
<td>22.1588</td>
<td>0.139</td>
<td>-0.307</td>
</tr>
</tbody>
</table>

Table 2: The chromatic co-ordinates ($L^*a^*b^*$) recorded on the studied pigment samples.

Figure 1: CIE $a^*$ (left) and $b^*$ (right) mean values registered on the studied pigments.
Table 3: EDAX elemental analysis (at %) obtained on the studied pigment samples.

<table>
<thead>
<tr>
<th>Atomic (%)</th>
<th>Blue</th>
<th>Green</th>
<th>Red</th>
<th>Yellow</th>
<th>Brown</th>
<th>Black</th>
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</thead>
<tbody>
<tr>
<td>Na</td>
<td>1.32</td>
<td>0.88</td>
<td>2.03</td>
<td>3.21</td>
<td>2.03</td>
<td>-</td>
</tr>
<tr>
<td>Mg</td>
<td>1.14</td>
<td>2.06</td>
<td>1.20</td>
<td>1.06</td>
<td>1.20</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>0.65</td>
<td>6.08</td>
<td>7.12</td>
<td>17.64</td>
<td>13.15</td>
<td>0.07</td>
</tr>
<tr>
<td>Si</td>
<td>55.25</td>
<td>66.06</td>
<td>61.02</td>
<td>46.03</td>
<td>38.17</td>
<td>0.09</td>
</tr>
<tr>
<td>S</td>
<td>3.72</td>
<td>8.15</td>
<td>4.15</td>
<td>7.13</td>
<td>14.15</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>21.04</td>
<td>8.21</td>
<td>2.21</td>
<td>12.28</td>
<td>16.21</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>0.23</td>
<td>0.63</td>
<td>1.2</td>
<td>0.98</td>
<td>1.2</td>
<td>-</td>
</tr>
<tr>
<td>Ti</td>
<td>1.1</td>
<td>0.62</td>
<td>0.62</td>
<td>1.20</td>
<td>0.62</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>1.20</td>
<td>1.02</td>
<td>20.45</td>
<td>11.47</td>
<td>9.75</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>14.35</td>
<td>6.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.52</td>
</tr>
<tr>
<td>L'</td>
<td>45.472</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a'</td>
<td>-11.654</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b'</td>
<td>-17.65</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Blue pigment

The observation of the reflectance spectrum curve registered on the blue pigment sample (Figure 2a) showed a sharp slope after a wavelength of 550 nm. Additionally, a characteristic absorption band at 640 nm was observed. This band is most probably attributed to the d-d transitions of Cu$^{2+}$ in the silicate sheet structure of the pigment [20]. The $a'$ and $b'$ average values recorded on the pigment were -11.698 and -16.690, respectively. The microscopic observations along with the negative $a'$ values showed that the sample tends to the green tone region. Figures 2b and 2c show the position of the studied area on the painted walls and the microscopic observation of some pigment grains with a green hue. According to previous studies, the amount of alkali (Natron salt or plant ash) and the firing temperature significantly control the produced colour of Egyptian blue. What’s more, the high alkali concentration in Egyptian blue results in a much greater hardness, thus, the pigment cannot be easily ground into a fine powder. Consequently, this affects strongly the hiding power of the pigment.

Figure 2: (a) Reflectance spectrum of the blue pigment and its microscopic characteristics, (b) the blue coloured area in the temple reliefs and, (c) the microscopic image of the pigment.

The microstructural investigation of cross-section on the sample, through ESEM, showed a heterogeneous distribution of large crystals (Figure 3). The EDAX elemental analysis showed elements
of silicon (Si), calcium (Ca) and copper (Cu) which are highly correlated to the mineral cuprorivaite (CaCuSi₄O₁₀). Egyptian blue is a synthetic pigment first appeared in Egypt during the third millennium BC [21]. In the crystal structure of the pigment, copper ions work as the key colouring agent [22]. And equally important, crystal aggregates contribute to enhancing the colour depth of the pigment [23].

**Green pigment**

The reflectance spectrum and the microscopic observations on the green pigment are shown in Figure 4. The reflectance spectrum showed a small slope at wavelength of 600 nm, then it started to show high reflectance intensity and shoulder beyond 650 nm. The $a^*$ and $b^*$ average values were (-14.588) and (2.478), respectively. The microscopic examinations on the sample shows a green silica-rich matrix with different hues. In fact, the firing temperature used in producing the pigment plays an important role to determining the final colour. Egyptian green with its turquoise colour, also refers to as Green Frit, is composed mainly of a silica-rich copper glass (green wollastonite) [24].

![Figure 3: Scanning electron micrograph (left) and EDAX spectrum (right) recorded on the sample.](image)

![Figure 4: Reflectance spectrum of the green pigment and its microscopic characteristics.](image)
**Yellow pigment**

The reflectance spectrum of the yellow pigment is recognized for the S-shape curve. A sharp positive slope at wavelengths lower than 600 nm suggests the occurrence of yellow ochre (Figure 5). The $a^*$ and $b^*$ values for the yellow sample were (9.682) and (26.870), respectively. Hydrated iron oxide (goethite, $\alpha$-FeOOH) is the main component of the pigment as well as clay minerals, silicates and calcium compounds [25]. It was long known that ochre owes its colour due to the Fe$^{3+}$ ion. Yellow ochre was a permanent colouring material in ancient Egypt [26]. In the Nile valley of Egypt, ochre occurs in the sandstones pockets as well as in the iron deposits in the Bahariya Oasis of the Western desert [27].

![Reflectance spectrum of the yellow pigment and its microscopic characteristics.](image)

**Red pigment**

For the red pigment, the reflectance spectrum showed an increase at 550–600 nm (Figure 6), and the band at 650 nm is for the Fe$^{3+}$ absorption in red ochre [28]. The $a^*$ and $b^*$ average values for the red sample were (32.774) and (22.297), respectively. The ESEM morphological study on the outer surface of the sample (Figure 7) showed clearly the fine aggregates of the pigment. Haematite ($\alpha$-Fe$_2$O$_3$), an iron (III)-oxide, is the main colouring agent in red ochre [29-30].

**Brown pigment**

In ancient Egypt, mixed pigments were used constantly to produce new hues or special tones in decorations [31]. For instance, the brown pigments were produced by adding carbon black, in different proportions, to ochre pigments. In the reflectance spectrum of the pigment (Figure 8), a flat spectral reflectance feature in the region (400–550 nm) was reported. The lightness ($L^*$) value showed an average of (34.0175), which ascertains the potential dark hue. Coupled with numerous observations, samples with dark colour have low intensity spectral reflectance and high $a^*$ values with an average of (20.786). Besides, the large size of pigment grains probably contributes in enhancing the dark tone. The large-sized grains affect dramatically the surface roughness leading to a destructive interference. Notably, the optical properties of pigments are influenced by the grains size, orientation and distribution of grains in the pictorial surface [32].
Figure 6: Reflectance spectrum of the red pigment and its microscopic characteristics.

L* = 50.432
a* = 32.542
b* = 23.423

Figure 7: ESEM micrograph obtained on the red pigment sample.

Figure 8: Reflectance spectrum of the brown pigment and its microscopic characteristics.

L* = 34.145
a* = 20.774
b* = 13.503
**Black pigment**

Regarding the black pigment, the lowest reflectance intensity was observed (Figure 9). The negative $a^*$ and $b^*$ values are correspond to the carbon black. The field observation to the site led to conclude that the black residues most probably attributed to soot layers. Fire hazards were common in ancient times due to human impacts. In fact, many restoration attempts to clean the temple walls have been undertaken. Taking into account the negative $b^*$ values of the sample, a blue hue was observed. Historically, soot was one of the oldest sources for the black colouring substances. As reported by Winter [33], carbon black, in attenuated layers, often reveals blue or brown tones. Additionally, the microscopic observations showed fine black grains on a bluish-green background.

![Figure 9: Reflectance spectrum of the black pigment and its microscopic characteristics.](image)

**Conclusions**

In the current study, colorimetric and spectral reflectance analysis were applied to study ancient pigments from the temple of Medinet Habu, Luxor, Upper Egypt. For cultural heritage objects, colour documentation provides valuable data on materials nature. A HunterLab spectrophotometer was used to record the $L^*a^*b^*$ values and the reflectance spectra of the studied pigments. Importantly, the microscopic observations and the morphological-microanalysis helped to characterizing the samples. The identified pigments were Egyptian blue (cuprorivaite), Egyptian green (copper wollastonite), yellow ochre, red ochre, brown pigment (a mixture of haematite and carbon black) and carbon black. Above all, the pigment identification was based on investigating the reflectance spectra, registered in the visible light region (400–700 nm), with the aid of some online databases\(^1\) together with some literature data in the field [34–36].

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\(^1\) e.g. [https://chsopensource.org/pigments-checker/](https://chsopensource.org/pigments-checker/) and [http://fors.ifac.cnr.it/main.php](http://fors.ifac.cnr.it/main.php)
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