Spectral Imaging of Ink Behind Glass: A Preliminary Investigation of the Colorimetric Shift

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Abstract

Transparent glass frames are often used to exhibit, handle, and store ancient manuscripts (folia or fragments) across museums, libraries, and collections. Once the manuscripts are carefully sealed (glazed), the process of re-opening the frame for the analysis of the glazed manuscript is not always desirable, given their fragile state of preservation. Therefore, micro-imaging with IR and UV light sources above the glass frame is a frequently used method for the preliminary (qualitative) classification of the inks applied on the manuscripts. Building on this well-established methodology, this study explores the potential of spectral imaging technology for the quantitative analysis of glazed manuscripts. The present research focuses on the colorimetric analysis of iron-gall and carbon black inks applied on a papyrus substrate, aiming to the quantitative analysis of the effect of glass frames to the acquired images. The obtained results show that the quantitative colorimetric analysis of the inks above the glass frame can be used for the preliminary classification of the inks, hence minimizing the need to open the glass frames for further analysis.

Introduction

Unbound folia or fragments of ancient papyrus manuscripts are commonly displayed and stored between two thin, transparent glass plates that are held tightly together with an adhesive tape [1]–[3]. These glass frames protect the sealed manuscript and, at the same time, permit the display and handling of the written surface(s). Various types of glass and adhesive tapes are used for this purpose, also referred to as “glazing”, across different collections. The choice of materials used for glazing is based on a series of factors, including the cost, display conditions and environmental factors, access to suppliers in different countries, and the impact of the housing method on the preservation of the manuscript [3]. Soda-lime glass (also known as window glass, float glass, or flat glass) is among the most popular choices and has been used traditionally across collections, while the properties of borosilicate glass, which presents higher resistance to fracturing and is chemically inert, have contributed to its increasing popularity in more recent years [1]–[3]. Glass frames with ultraviolet (UV) radiation protective filters are considered necessary for papyri that are exposed to daylight, e.g., when they are on display. Finally, and especially when it comes to parchment manuscripts, archival polyester pockets or sleeves are also a favourable storage method since they are chemically inert, easy to handle, and prohibit the development of mold.

Once the papyrus fragments are securely sealed between glass, and given their fragile state of preservation, curators are often reasonably hesitant to re-open the frames for materials analysis. Therefore, the use of portable USB microscopes (DinoLite), equipped with UV and infrared (IR) and external visual (Vis) light sources, above the glass frame, a technique that has been developed by the Bundesanstalt für Materialforschung und -prüfung (BAM, Berlin, Germany) and the Centre for the Study of Manuscript Cultures (CSMC, Hamburg, Germany), is now established as a successful and effective method for the preliminary characterisation of the applied inks [4], [5]. The methodology is based on the distinguishable optical properties of the three main classes of inks: namely carbon-based, plant-based, and metallogallic inks [6]. Carbon-based black inks remain opaque across the spectrum, iron gall inks become increasingly transparent under IR illumination, and plant-based inks tend to disappear, i.e., become completely transparent, at approximately 740 nm [4], [5]. Therefore, through the comparison of the opacity and thickness of the written lines, information about the composition of the inks can be extracted.

The above approach allows for the rapid scan of the manuscript above the glass frames to successfully pursue the qualitative classification of the three main classes of inks and can therefore guide further research that may include the chemical analysis of selected samples. However, since what is compared here is the obtained micrographs, the technique relies on the rather subjective ability of the researcher to recognize the variations in terms of thickness and opacity between the three modes of illumination, which are predefined by the DinoLite manufacturer: a) under white light; b) at 390 nm (UV), and c) at 940 nm (NIR). Therefore, the preliminary characterisation of the inks relies on the descriptive study of the obtained micrographs, while the impact of glass is not quantified.

Considering the need to minimize the unnecessary opening of sealed or encapsulated manuscripts, this study aims to quantify the effect of glass and polyester sheets on measurements made through the framing materials, by means of imaging. At this preliminary stage of our study, we have limited our scope to colorimetric analysis, focusing on information coming from the visible range, to assess the impact of glass and polyester pockets to the obtained results. For this purpose, we have produced reference samples (mock-ups) by applying carbon-black and iron gall ink on a papyrus substrate. Additionally, the behaviour of red earth pigment was studied for comparison. Being able to quantify the impact of glass frames will reduce the need to remove papyri from their frames, making imaging a potential quantitative methodological tool for the analysis of papyri that are especially fragile.

Materials and Methods

Sample preparation

For this initial stage of the research, we decided to limit our focus to the colorimetric analysis of known samples and the study of the impact of soda-lime and archival polyester pockets on the obtained results. For this purpose, we used polyester pockets (Secol Limited, Thetford, UK) and soda-lime glass sheets that are used to house papyri at the Papyrus Collection of the University of Oslo Library.

Crucial for this stage of our study was the direct communication of our research. Therefore, we decided to directly share the process with a wider audience through a series of blog posts [7]–[9]. At the same time, we decided to involve individuals with varied backgrounds (artistic practice, classical philology and papyrology, computer science) in the process of sample preparation and image acquisition, and to directly explore the intersection of these disciplines.

Carbon-black, iron gall, and red earth inks were produced following well-documented and reproducible recipes with commercially available starting materials. The production process is beyond the scope of the present paper, for details: [8], [9]. The inks were applied on commercially available papyrus (Römer Shop, Germany). Each participant of the pilot study produced a series of mock-ups applying the produced inks on papyrus, parchment, and acid-free paper, exploring the workability and properties of the produced inks on different substrates.

The prepared mock-ups were analysed under three different experimental set-ups: without glass, placed in-between two soda-lime glass sheets, and in the polyester pocket. Here we present the results obtained from the analysis of papyrus written with iron gall ink, carbon ink, and a commercially available red earth ink (**Figure 1**).

Figure 1. *An example of the acquired image and its corresponding reference image obtained by manual labelling.*

Image acquisition

The image acquisition was carried out using a Specim IQ hyperspectral camera positioned at a perpendicular angle to the normal surface of the papyrus. A 200-watt halogen lamp was used as the illumination, positioned at approximately the same height as the camera, and at a 45° angle to the normal surface of the object. The angle and distance between the object and the light source were optimized to minimize specular reflection and the impact of heat. A calibration target is always placed next to and imaged together with the object of interest.

Data

Each image acquisition results in a spectral image of 500×500 pixels, represented in terms of spectral reflectance. The spectral dimension is 186 bands from approximately 400-1000 nm, spaced in approximately 2.88 nm intervals. Since this paper focuses on the colorimetric analyses of the results, the spectral reflectance data are converted to the CIELAB colour space, assuming D65 illumination and CIE Colour Matching Function 2° Standard Observer.

In total, there are three images obtained from 1) the unframed papyrus, 2) the papyrus placed in-between the soda-lime glass sheets, and 3) in the polyester pocket. A reference image is produced from each acquired image by manual labelling (see **Figure 1**). This reference image provides information about whether a pixel belongs to a specific ink.

Data analysis: Mahalanobis distance (MD)

This measure is used to quantify the shift impacting the colorimetric values of the framed papyri due to the presence of either glass or the polyester film. Since we are measuring the shift, the distribution of colorimetric values of unframed papyri will be used as reference. MD measures the likelihood of a point belonging to a distribution. Therefore, all pixel values corresponding to inks obtained from the measurements of the framed papyri will return a distance value.

MD values can be considered as z-scores for the multivariate domain. Assuming a normal distribution, we will use the empirical law, which states that 99.7% of the population lies within three standard deviations from the mean of the distribution. Following the methodology detailed elsewhere [10], [11], we will use the median instead of the mean of the distribution as the estimator of the center of the distribution. The median calculation is performed in the spectral reflectance space and then converted to the CIELAB colour space. Then, the MD is computed directly in the CIELAB space instead of the spectral reflectance space.

Results

In the following, the colorimetric results are presented and discussed for each ink (iron gall, carbon-based, and red earth). In each case, the analyses of their pixel distribution will be given and discussed. The plotted results show the distribution of colorimetric values in the CIELAB colour space. Explanations allowing the interpretation of them are given in **Table 1**.

Table 1. Supplementary information regarding the visual components of **Figure 2, Figure 3, and Figure 4**, necessary to allow their observation and interpretation.

L* axis	Represents lightness values. A change in L* indicates a change in the blackness of an ink, e.g., darker, or lighter black.
a* and b* axes	Represent chromaticity values. A change in a* or b* values would mean a change in chroma (e.g., red to less vivid red) or hue (e.g., brown or blue inks).
Red dot	The median of the distribution corresponding to pixels from the unframed papyrus.
Convex hull	The line marking the area of a distribution, computed by connecting the outermost points in each distribution. It visualises the shape and extent of a distribution.

Iron gall ink

Figure 2 shows the colorimetric distribution of freshly made iron gall ink imaged 1) directly (unframed papyrus), 2) placed in-between the soda-lime glass sheets, and 3) in the polyester protective pocket. The general trend that can be observed is that the framed papyrus presents a smaller colorimetric distribution compared to the unframed papyrus. The convex hulls of the framed papyri are also mostly contained within the extent of the unframed papyrus.

If we look at especially the a*b* plots, there are a few points in the framed papyrus that lie outside the convex hull of the unframed one. However, they do not represent the majority of the points and should therefore be considered outliers. There is also a slight shift in the convex hull of the framed papyrus relative to

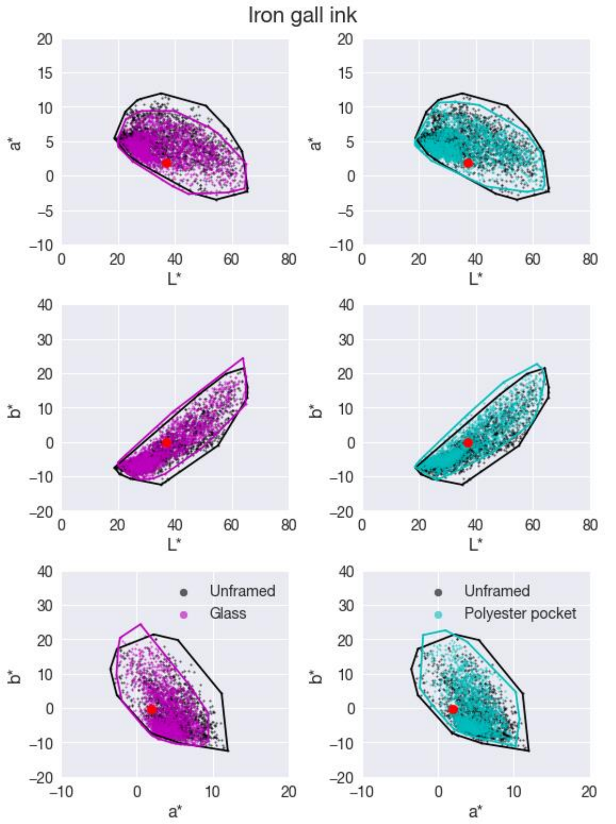

Figure 2. *Colorimetric distribution of iron gall ink pixels in the CIELAB color space. The pixels are obtained directly from the object, and when it is placed 1) between glass sheets or 2) in a polyester pocket. The convex hull of each distribution is also plotted; it represents the area of the distribution, connecting its outermost data points. The red dot represents the median point of the pixel distribution of the unframed papyrus.*

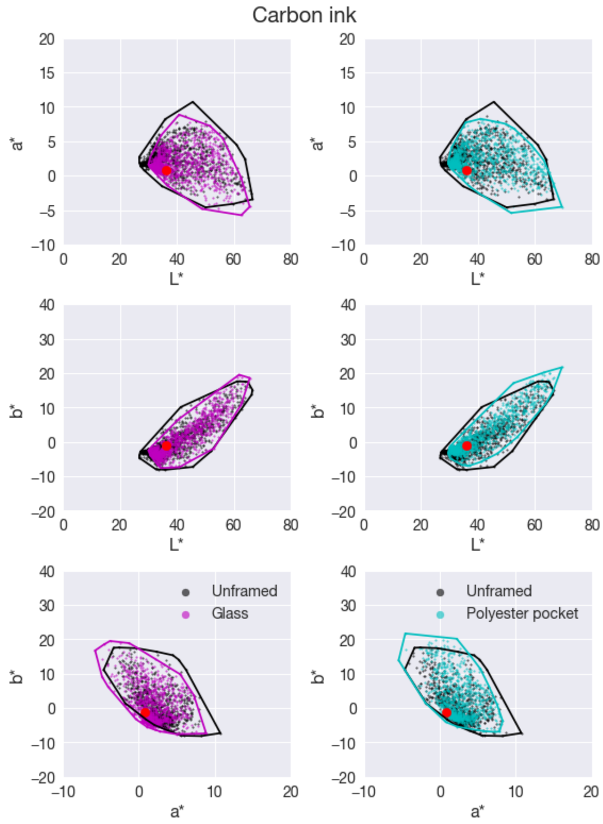

Figure 3. *Colorimetric distribution of carbon ink pixels in the CIELAB color space. The pixels are obtained directly from the object, and when it is placed in between 1) glass sheets or 2) a polyester pocket.*

the unframed one along the L* axis. These observations suggest that the effect the glass frames and polyester pockets to the colorimetric values of iron gall ink is reserved to a slight shift in lightness and reduced chromaticity. Comparing the two housing media, i.e., glass vs. polyester, a greater shrinkage is observed for the glass frame than to the polyester pocket.

Table 2 provides complementary statistical analysis to the plotted observations of **Figure 2**, by means of MD. Note that the unit of these MD values is one standard deviation of the distribution of the unframed iron gall ink pixels. On average, the pixel values corresponding to the samples in the glass frame and the polyester pocket are located around 1.78 and 1.86 units, respectively. This is a decrease from the 2.02 value obtained from the unframed papyri. Moreover, the minimum and maximum values of the framed papyri demonstrate a shrink in the range of values compared to the unframed one. If a normal distribution is assumed and the empirical rule applied, we can compute the percentage of outliers in the distribution of pixel values. This means that all pixels with MD > 3 are considered outliers. Here, too, we can observe a decrease in the percentage of outliers for the framed papyrus. In agreement with the observation made in the plots of **Figure 2**, we see that the glass frame shrinks the colorimetric distribution of pixel values compared to the polyester pocket.

Table 2. *Statistical analysis of the colorimetric distribution of iron gall ink, imaged without a frame, behind a glass frame or polyester pocket, by means of Mahalanobis distance (MD). The unit in this MD is 1 standard deviation of the distribution of iron gall ink pixels imaged directly (unframed).*

Frame type	**Mahalanobis distance (MD)**			
	Average	**Min.**	**Max.**	**% of outliers**
-	2.02	0.0	5.60	15.40
Glass	1.78	0.24	5.17	9.61
Polyester pocket	1.86	0.16	5.35	12.55

Carbon black ink

The distribution of the colorimetric values obtained for carbon ink is shown in **Figure 3**. Compared to iron gall ink, here the lightness shift becomes clearer, see L*a* and L*b* plots. However, instead of a shrink in chromaticity, we can observe a clear shift in the distribution, especially in the a*b* plots. As the observation for iron gall ink, the glass frame also causes a slightly more compact distribution, i.e., smaller convex hull, than the polyester pocket.

The measure of outliers is a good indicator of colorimetric shift in this work, since we always calculate MD relative to the distribution of the unframed papyrus. A larger shift means it becomes less likely for the pixels to belong to the distribution of the unframed papyrus, thus larger percentage of outliers.

Table 3 shows that the sample in the polyester pocket has more outliers than the glass framed one, even exceeding the unframed papyrus. The larger average, minimum, and maximum values compared to the unframed papyrus suggest that the polyester pocket shifts the pixel distribution further away from the unframed papyrus.

Table 3. *Statistical analysis of the colorimetric distribution of carbon ink, imaged without a frame, behind a glass frame or polyester pocket, by means of MD. The unit in this MD is 1 standard deviation of the distribution of carbon ink pixels imaged directly (unframed).*

Frame type	**Mahalanobis distance (MD)**			
	Average	**Min.**	**Max.**	**% of outliers**
-	1.70	0.0	6.36	14.31
Glass	1.42	0.11	5.85	9.88
Polyester pocket	1.84	0.18	6.60	19.57

Red earth pigment

Finally, the colorimetric distribution for the red earth pigment is presented in **Figure 4**. The range of values are different from those of the iron gall and carbon inks, i.e., **Figure 2** and **Figure 3**, respectively. Nevertheless, compared to the black inks, the shift in colorimetric distribution for this red pigment is evident and easily observable in terms of both lightness (L* axis) and chromaticity (a* and b* axes).

The main difference observed between the impact of the housing media on the colorimetric values is that while glass shifts and shrinks the pixel distribution, the effect of polyester is reserved to shifting the distribution. In terms of lightness (L*), the shift tends toward lower values, suggesting a darkening effect to the red pigment. The shift in chromaticity values occurs along the a* axis, i.e., the axis that is relative to the green-red opponent colours, which remain in the positive quadrant. This shift is observed to a larger degree in the case of polyester pocket compared to the glass. The direct interpretation of this result is that red pigments will appear to be less saturated when observed (or measured) through archival polyester pockets, compared to the observations made through glass.

The statistical analysis of the results, presented in **Table 4**, confirms the observations of the plotted results (**Figure 4**): the colorimetric shift in the distribution is larger compared to the two black inks. The percentage of outliers for the measurements carried out through glass or polyester is significantly larger compared to the unframed sample. At the same time, the observed differences between the two types of frames are smaller. The shift of the convex hulls is also confirmed by the statistical results, since the average, minimum, and maximum values of the framed papyrus are higher than the unframed one.

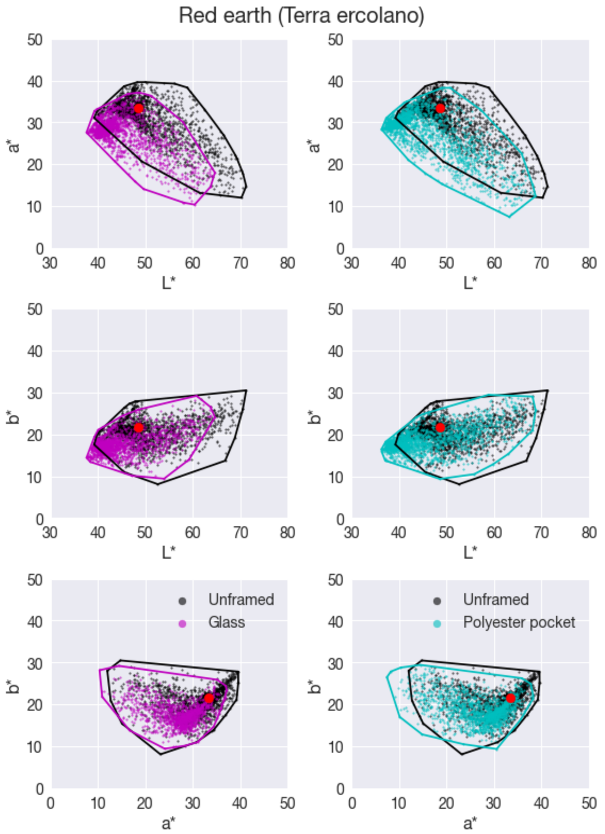

Figure 4. *Colorimetric distribution of the pixels of the red earth pigment in the CIELAB color space. The pixels are obtained directly from the object, and when it is placed in between 1) glass sheets or 2) a polyester pocket.*

Table 4. *Statistical analysis of the colorimetric distribution of red earth pigment (terra ercolano), imaged without and with frame (glass or polyester pocket), by means of MD. The unit in this MD is 1 standard deviation of the distribution of red pigment pixels imaged directly (unframed).*

Frame type	**Mahalanobis distance (MD)**			
	Average	**Min.**	**Max.**	**% of outliers**
-	1.57	0.0	5.63	8.58
Glass	2.54	0.18	5.77	30.28
Polyester pocket	2.55	0.21	5.75	31.17

Discussion and Conclusions

This paper focuses on the preliminary investigation of the impact of housing media to the image acquisition of ancient manuscripts. At this pilot stage, we limited the scope of our research to papyrus substrate and only three reference materials (carbon-based black ink, iron gall ink, and red earth) and two housing media (soda-lime glass sheets and archival polyester pockets, two popular methods of storing and handling manuscripts). Moreover, we have limited the data analysis to the visible spectrum, focusing on the analysis of the colorimetric shift under different acquisition conditions (i.e., with or without a medium between the sensor and the sample). The general trend observed among the obtained results suggest that the use of both glass and polyester pockets as framing options reduce the variability of the colorimetric values.

As demonstrated in the previous section, the impact of the glass and polyester on the colorimetric results is quantifiable. The quantification of this impact on imaging reduces the need to expose ancient manuscripts and minimizes unnecessary potential harm, establishing therefore imaging as a methodology for the preliminary analysis of manuscripts that are especially fragile through their housing solution. Even though imaging cannot provide conclusive results regarding the chemical composition of the inks used in ancient manuscripts, the preliminary classification and clustering of the materials can be beneficial for decision making regarding further analytical investigations.

However, further research is necessary to establish the proposed methodology. Therefore, we aim to expand our study beyond colorimetry and to include the analysis of spectral data since the inks present interesting behaviour in the near-infrared (NIR) spectral region [5], [6], [12]. Moreover, the impact of different types of archival housing solutions used across manuscript collections (e.g., borosilicate glass, UV protected glass) will be analysed. Finally, before moving our research to ancient manuscripts, we need to assess the impact of the heat generated by the external illumination source to the manuscripts under glass.

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