

Quantitative approaches for Fiber Optics Reflectance Spectroscopy (FORS)

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Abstract – In this paper, Fiber Optics Reflectance Spectroscopy (FORS) was used to measure the concentration of pigments in paintings on a paper substrate. There is currently no agreement on a general quantitative approach using FORS, even if several attempts have been made in the past with varying degrees of success. In our approach, reflectance spectra were processed using the Kubelka-Munk (K-M) theoretical model of light propagation in an optical inhomogeneous medium. Experimental tests were carried out on mock-ups prepared using mixtures of two pigments (ultramarine blue and Naples yellow) and their reflectance spectra were acquired using a set-up with an integrating sphere. Given the linear relationship between the scattering and absorption coefficients of the pigments, and knowing the volume concentration of the pigments, the method enables both identification and quantification of components in the binary paint mixtures from FORS spectra.

I. INTRODUCTION

Fiber Optics Reflectance Spectroscopy (FORS) is a non-invasive method that can be used for the identification of colorants, as well as the substrates, that can be found in paintings and manuscripts [1–4]. The qualitative study of colorants on parchment, or watercolors on paper, with FORS is well established and widespread [5, 6]. This technique is capable of acquiring hundreds of reflectance spectra *in situ* in a relatively short time, providing a portable and relatively inexpensive diagnostic technique.

In the past, the quantitative study of the concentration of the pigments in mixtures in paintings was attempted using various mathematical approaches [7–9]. These approaches are based on the Kubelka-Munk theory (K-M), a simplified model for the radiation transfer in optically inhomogeneous layers. However, the nonlinearity of the reflectance

spectra of pigment mixtures represents an obstacle for the mathematical analysis of the acquired spectra [5, 10, 11]. Therefore, no general and easy methodologies have been established over the years as a reference to perform such calculations.

This paper focuses on optimizing the FORS experimental setup for the quantitative measurement of pigment concentrations in binary mixtures applied to paper-based paintings. Mock-ups were prepared using pigments commonly found in paintings and illuminated manuscripts to evaluate the accuracy of the K-M approach in modeling the reflectance of mixed paint layers.

II. MATHEMATICAL PROCEDURE

The intrinsic reflectance, R_∞ , that would have a painting layer with infinite optical thickness, is obtained by measuring four separate reflectance spectra of: *i*) a white reference, R_w ; *ii*) a black reference, R_b ; *iii*) the sample on top of the white reference, R_{sw} ; and *iv*) the sample on top of the black reference, R_{sb} [2, 12, 13]. Then:

$$R_\infty = a - \sqrt{a^2 - 1} \quad (1)$$

where

$$a = \frac{(R_w - R_b)(1 + R_{sw}R_{sb}) - (R_{sw} - R_{sb})(1 + R_wR_b)}{2(R_wR_{sb} - R_bR_{sw})} \quad (2)$$

From R_∞ , it is possible to calculate the so-called K-M pseudo-absorption or remission function:

$$A_{KM} = \frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (3)$$

where K and S are the phenomenological absorption and scattering coefficients, respectively, of the painted layer, and can be obtained given the thickness of the sample, t ,

by calculating:

$$S = \frac{1}{t \left(\frac{1}{R_\infty} - R_\infty \right)} \ln \frac{(1 - R_b R_\infty)(R_\infty - R_{sw})}{(1 - R_{sw} R_\infty)(R_\infty - R_b)} \quad (4)$$

while Equation 3 can be used to obtain K . These values represent the amount of radiation absorbed and the amount of radiation scattered per length unit within the optical inhomogeneous layer. The reconstruction of the reflectance spectra of a painting made of a binary mixture can be performed using the K and S parameters.

It should be noted that these parameters take into account the paper morphology after painting application, which could be modified by soaking with fresh paint or in the case of watercolor.

Duncan showed in 1940 that the K and S coefficients are additive in a mixture in proportion to the volume concentrations of the pigments in the paint layer [14]. Thus:

$$\frac{K_m}{S_m} = \frac{c_1 K_1 + c_2 K_2 + \dots + c_n K_n}{c_1 S_1 + c_2 S_2 + \dots + c_n S_n} \quad (5)$$

where K_m and S_m are the coefficients of the mixture, K_i and S_i are the values related to the pigment specified by $i = 1, 2, \dots, n$, and c_i is the volume concentration of the pigment in the mixture, with $c_1 + c_2 + \dots + c_n = 1$.

For a binary mixture, Equation 5 can be rewritten as

$$\frac{K_m}{S_m} = \frac{c_1 K_1 + (1 - c_1) K_2}{c_1 S_1 + (1 - c_1) S_2} \quad (6)$$

Once the parameters K_m and S_m of the mixture are known, it is possible to recover the reflectance of the mixture from Equation 3, that can be expressed:

$$R_\infty = 1 + \frac{K_m}{S_m} - \sqrt{\left(\frac{K_m}{S_m} \right)^2 + 2 \frac{K_m}{S_m}} \quad (7)$$

A numerical approach based on the simulation and comparison of gouache mixtures—using the original K-M theory and reflectance measurements of pure and binary samples—was developed by G. Dupuis and M. Menu in 2006 [8]. Although the method yielded promising results, some limitations remained, particularly regarding the identification of certain pigment combinations.

III. EXPERIMENTAL METHOD

A. Materials

In this study we experimentally test mock-ups prepared not using two gouaches but mixtures of two inorganic pigments (ultramarine blue and Naples yellow). In order to analyse the viability of performing quantitative analysis using FORS, mock-ups reference paintings were prepared in collaboration with the National Central Library of Rome (BNCR).

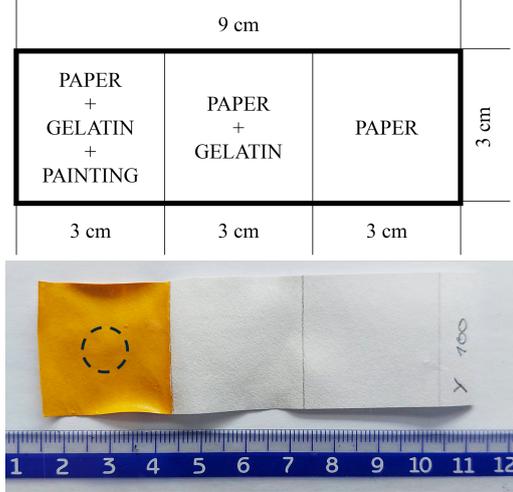


Fig. 1. Schematic of the samples (top) and sample Y100 (bottom). The dashed circle represents the area measured for each sample by using the integrating sphere.

Stripes of Whatman paper n.1, 3 cm × 9 cm in size, were used as substrates with gelatin sizing (Fig. 1). The gelatin (gel strength ~225 g Bloom, Type B, SIGMA, Life Science, Germany) applied to the paper was derived from bovine skin. The pigments selected for the experiment are from Poggi S.r.l (Italy):

1. Ultramarine Pure Blue (polysulfide of sodium aluminosilicate, $\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$, PB29).
2. Naples Yellow (cadmium sulfide+ iron oxide, $\text{CdS} + \text{Fe}_2\text{O}_3$, PY35 + PY42).

Ultramarine Blue will be referred to as Blue (B), and Naples Yellow as Yellow (Y) throughout the paper.

The pigments were mixed with a 30% gum arabic solution (used as a binder) at a pigment-to-binder ratio of 1:16, and then applied on the paper. The gum arabic, in granular form, was sourced from Antares S.r.l. (Italy). These proportions were selected to ensure partial transparency of the samples across the entire measured spectral range, a necessary condition for the applicability of Equations 2 and 4 [2].

The samples have one section for each of the different layers applied to the paper, and for the paper itself (Fig. 1), in order to check any optical influence from the substrate. Different binary combinations of B+Y were prepared with three volume concentrations (25%–75%, 50%–50% and 75%–25%) and subsequently mixed with the gum arabic. The samples prepared with pure pigments are coded as X100, being X the label of the color. The ones prepared with a mixture appear as $X_{c_X} + Y_{c_Y}$, where X and Y represent the colors and c_X and c_Y their relative volume concentrations.

After the paintings had dried, t was measured for each sample using a mechanical micrometer with 0.001 mm resolution. The values include the thickness of the paper, which absorbed part of the painting, and that of the layer remaining on the surface.

B. FORS set-up

Ultraviolet (UV), visible (Vis) and near infrared (NIR) diffuse reflectance spectra were measured using a portable set-up from Avantes BV (The Netherlands). In this set-up, radiation is emitted from a combined deuterium-halogen AvaLight-DH-S-BAL light source. This is connected by a 800 μm diameter solarized optical fiber (model FC-UV800-2-SR) to a 50 mm diameter Spectralon coated integrating sphere (model AvaSphere-50-REFL). This integrating sphere is used to illuminate the sample and collect radiation scattered from the painting surface from all angles. The integrating sphere sample port is 10 mm in diameter and it has a gloss trap to avoid specular reflectance from the samples. From the integrating sphere, radiation is sent by a 600 μm diameter optical fiber (model FC-UV600-2) to an AvaSpec-2048 \times 14-USB2 spectrometer equipped with a 2048 \times 14 pixels CCD detector. The use of the integrating sphere prevents the distance from the sample to the fiber and its numerical aperture to have any effect on spectral data from a region. The spectrometer's diffraction grating allows measurements in the 250–1050 nm range with a spectral resolution of 4.3 nm. Data acquisition was controlled by a personal computer.

UV-Vis-NIR spectra were acquired with the samples placed first on a white Spectralon reference (99% reflectance) and subsequently on a black Spectralon reference (2% reflectance). The reproducibility of the measurements was ensured by placing on top of the samples a semi-transparent reference mask with a circular aperture for the integrating sphere sample port. In this way, the measured area was the same for each of the samples (Fig. 1). The data were processed according to the K-M theory using custom programs written in Wolfram Mathematica [15], and the results were plotted using OriginPro [16].

IV. RESULTS

From the reflectance spectra of the samples, the corresponding R_∞ values were calculated using Equations 1 and 2. The spectra of the samples prepared with pure B and Y pigments are shown in Fig. 2. Their spectral shapes closely match those reported in the literature [5] and other databases such as the IFAC-CNR Spectroscopic Measurement Database and the Pigments Checker STANDARD v.5 of the CHSOS. The B spectrum shows a reflectance maximum at about 450 nm, a very strong absorption at about 590 nm and an inflexion point at 710 nm. The Y spectrum shows a main inflexion point at about 520 nm and a minor one at 480 nm. The latter possibly appears due to the fact

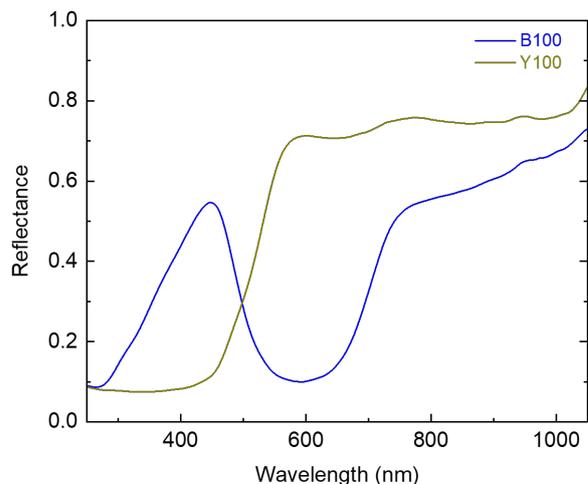


Fig. 2. Reflectance spectra of the samples B100 (blue curve) and Y100 (dark yellow curve) prepared with pure pigments.

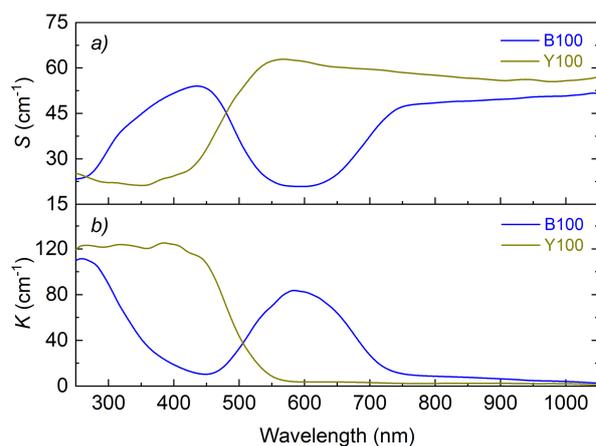


Fig. 3. Scattering S (a) and absorption K (b) coefficients of samples B100 (blue curve) and Y100 (dark yellow curve).

that Y is a mixture of cadmium sulfide and iron oxide.

The scattering and absorption coefficients, S and K , were obtained using Equations 3 and 4. These are shown in Fig. 3. The K spectrum of the B pigment shows an absorption maxima at 590 nm, in agreement with the reflectance spectrum. The K spectrum of the Y pigment shows a steady decrease from 560 nm on and an absorption plateau below 450 nm. The S spectra show spectral shapes with approximately opposite behaviors with respect K spectra.

Finally, R_∞ was calculated by combining the individual S and K values of the pure pigments with the nominal volume concentration used for the mixtures (Fig. 4). The mixing spectra appear to be nonlinearly dependent on the reflectance of each pure pigments.

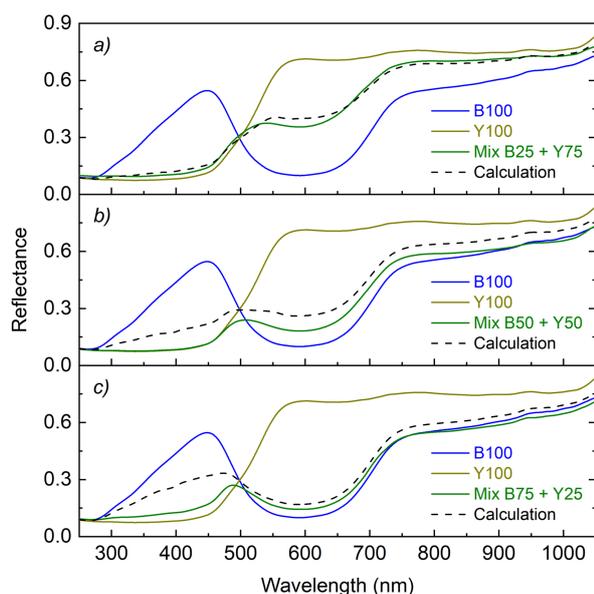


Fig. 4. Reflectance spectra of the samples prepared with mixtures of B (blue curve) and Y (dark yellow curve) pigments. The black dashed line represents the mathematical reconstruction based on Equation 7. The green curves show the measured reflectance of the mixtures with 25% of B and 75% of Y (a), 50% of B and 50% of Y (b), and 75% of B and 25% of Y (c).

As evident from the Fig. 4, the agreement between the reflectance calculated using the nominal volume concentrations (black dashed curve) and the reflectance measured on the mock-ups with 25%–75%, 50%–50% and 75%–25% volume concentrations (green curves) is very good. The small discrepancy observed in the UV range for the B75+Y25 sample can be explained by the absorption contribution in this spectral range of the gum arabic used as a binder, which is not considered in the mathematical procedure [17]. For samples B25+Y75 and B50+Y50, instead, the high optical absorption of the Y pigment in the UV range decreases the gum arabic contribution, improving the agreement. This validates the proposed method to recover the volume concentration of pigments in a mixture, and paves the way for future developments in the quantitative analysis of pigment mixtures.

V. CONCLUSIONS

The results obtained in this study demonstrate that it is possible to reproduce the reflectance spectra of binary pigment mixtures on paper substrates. This is a promising outcome that supports further developments of the mathematical procedure.

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