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Optical and colorimetric characterization on binary mixtures prepared with coloured and white historical pigments

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ABSTRACT

The main goal of the paper is the optical and colorimetric characterization of the pigment mixtures realized with pure pigments of the principal artist's hues and white pigments through spectrophotometric analysis. This research work represents a first step in a methodology study aimed to the verify potentialities and limits of spectrophotometric techniques in the identification of pigments in mixtures. The analysis regarded the trend of Spectral Reflectance Factor (SRF%) in visible spectrum and of the derivative of SRF, d(SRF%). In particular, the analysis of d(SRF%) of the mixture in the function of achromatic pigment concentration has the aim of highlight shift of the *extrema* points in relation to the relative quantities of the mixture components.

To this aim, painting samples were prepared in laboratory mixing the coloured pigments with achromatic ones in variable weight concentration from 10% to 90% for each of the components. This is necessary to evaluate the *minimum* quantities of white that could change the coloured pigments SRF% spectra. Also the analysis of colour coordinates is performed to put in evidence the L*, a*, b* trend in CIELAB 1976 space.

1. Introduction

This research work is part of a wide research project having as goal the historical pigment mixtures investigation. In particular, in this occasion, the binary mixtures between pure pigments and white ones are analysed. This represents a first step in a methodology study aimed to the verify potentialities and limits of spectrophotometric analysis in the qualitative identification of pigments in mixtures.

In the past, paintings were made according to two types of pigment mixtures. The first one mixing two different hues of the three primary colours to obtain secondaries and/or tertiaries and the second one with white or black pigments in order to get different tints [1]. About this last one, a colour can be altered in three ways by tinting, shading and toning. Tints mean adding white to a coloured pigment. This leads to less saturation making hue less intense. Artists often add a tiny touch of white to a pure pigment. Shades are created when only black is added to a hue. Many black pigments change a lot the hue even in a small amount, so they are used sparingly. Alternatively, a hue can often be made darker by adding another dark hue rather than black.

Tones are created when both black and white (that is grey) are added to a hue. Depending on the proportions of black, white and the original hue used, tones can be darker or lighter than the original one [1].

However, mixing a pigment with one other (chromatic and achromatic) causes losing of its “chromatic footprint”. This losing is very interesting and requires a deepened knowledge.

The mixtures of pigments used in paintings are object of several studies from different points of view and with different techniques among which spectrophotometry. In particular, spectrophotometric analysis in visible range is based on the study of Spectral Reflectance Factor (SRF%) trend in the range of electromagnetic spectrum between 400 and 700 nm. The behaviour of SRF% provides information about the optical characteristics of a material and it can useful to identify it and to specify its colours [2]. Furthermore, when a reflectance spectrum from an object's surface is recorded under standard operative conditions, the spectral curve can be used for the quantitative measurement of colour. By the integration of SRF% curves, in fact, software processes calculate the colour coordinates in a selected space codified by CIE (*Commission Internationale de l'Eclairage*). The spectrophotometer is not the only instrument that can give us the colour coordinates. It is possible to determine them also using a colorimeter. In the science of colour measurements, these two instruments provide a set of standardized conditions that help assure consistency and repeatability but they have to be distinguish because are different in the method with which

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Table 1
The pigments of the principal hues and the white ones.

ID code	Name	Chemical Description	Colour Index
R1	Cinnabar	HgS	PR 106.77766
R2	Red Ochre	$Fe_2O_3{\cdot}nH_2O$	PR 102.77491
R3	Hematite	Fe_2O_3	PR 102.77491
Y1	Dark lead-tin Yellow	Pb_2SnO_4 o $PbSn_2{\cdot}SiO_7$	PY-41.77629
Y2	Yellow Ochre	$Fe(OH)_3$	PY 43.77492
Y3	Natural Sienna earth	$Fe_2O_3{\cdot}nH_2O + MnO_2 + Al_2O_3{\cdot}SiO_2{\cdot}2(H_2O)$	PY 43.77492
B1	Natural Ultramarine Blue	$3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}Na_2S$	PB 29.77007
B2	Synthetic Ultramarine Blue	$2Na_2Al_2Si_2O_6{\cdot}NaS2$	PB 29.77007
B3	Indigo Blue	$C_{16}H_{10}O_2N_2$	NB 1.75780
G1	Verona Green earth	Al-, K-, Mg-, Ca-, Fe-Silicate	PG 23.77009
G2	Malachite	$2CuCO_3{\cdot}Cu(OH)_2$	PB 30.77420
G3	Crysocolla	$CuSiO_3$	PB 31.77437
W	Bone White	$Ca_3(PO_4)_2$	N/A
Zn	Zinc White	ZnO	PW-4
Ti	Titanium White	TiO_2	PW-6

colour is measured.

In colorimetry, the quantification of colour is based on the three-component theory of colour vision, which states that the human eye possesses receptors for three primary colours (red, green and blue) and that all colours are seen as mixtures of these primaries. Colorimeters, based on this theory of colour perception, employ three photocells as receptors to see colour in much the same way as the human eye [3]. Spectrophotometry, on the other hand, uses many more sensors to separate a beam of reflected or transmitted light into its component wavelengths. It measures the spectral reflectance at each wavelength on the visible spectrum continuum that permit to identify a specific pigment. From a qualitative point of view, using spectrophotometric technique, the possibility of identifying pigment is connected to the comparison between data acquired and ones stored on specific database [4,5].

Some research works debate about the problem of the identification of pigments in mixtures with spectrophotometric analysis [6–13] and researchers have been involved in studies of pigment mixtures, also with achromatic ones [14–18]. In particular, in the last years, derivate curves, calculated from the reflectance spectra, are used to better study the spectral behaviour of the pigment in the visible region. The identification of *extrema* point in the SRF% derivate spectra allow to differentiate pigments [19–21]. Although the idea of taking into account the reflectance derivatives was proposed several decades ago, even today the use of derivatives, first and/or second, is an open question [21–29].

Other studies were performed about the quantitative determination of the component of a mixture using mixing model [27,30–34].

To achieve the main goal of the research work representing by optical and colorimetric study of the mixtures constituted by historical pigments, painting samples were prepared in laboratory mixing with fixed proportion coloured and white pigments in fixed ratio with one of the most used historical vehicle, egg tempera. The choose white pigments are “Bone white”, “Zinc white” and “Titanium white”. The first one is an historical pigment while the second ones, are synthetic pigments, predominantly used in restoration [35,36].

A further objective of the work is the improvement of the database of historical pigments and mixtures available at PH3DRA (*PHysics for Dating Diagnostics Dosimetry Research and Applications*) labs.

With the same goal, previous papers focused on the influence of particle sizes and of vehicles on historical pigments optical characterization have been published [37–40].

2. Material and methods

2.1. The samples

The artist's palette in the past was generally constituted by pigments corresponding of red, yellow, blue and green colours with addition of black and white [1,41]. In this paper these colours are indicated as “artist's hues”.

The pigments selected for the study are documented in the historical fonts and in restoration manuals [36,42–45]. They were listed in Table 1, for the artist's hues, Red (R), Yellow (Y), Blue (B) and Green (G), along the IDentification (ID) code, the name, the related chemical description provided by the supplier and the Colour Index (CI).

In the same Table the white pigments selected for the study are reported. They are of two principal types. The bone white is a natural pigment obtained from bone calcination and Zinc and Titanium whites are artificially made. They were extensively used starting from the end of the XVIII century [35], also in restoration.

The pigments, purchased by Zecchi company [46], were supplied in state of powder, dry bulk solid composed of loose particles. The pigment powder, with diameter belonging to $45 < \Phi < 75\,\mu m$, was used for the paint sample preparation. The particle size pigments selection was made by mechanical sieving using stainless steel mesh of different sizes.

The paints were prepared mixing the pigments in variable weight from 10% to 90% for each component. The binary mixtures, as obtained, were mixed with wet *medium* (vehicle) with a fixed ratio equal to 1:3 between powdered pigments mixtures and vehicle. The selected historical *medium* was egg tempera [36].

All paints were obtained by brushing the mixtures on canvas prepared with synthetic gypsum [36] completely obscuring the support in order to obtain opaque samples with a mass tone as defined by Mayer [1].

2.2. The spectrophotometric analysis

The analysis was conducted using a Konica Minolta® spectrophotometer, model CM-2600d with measurement geometry d/8°, selecting an area of 6 mm in diameter (SAV, *Small Average Value*) following a standard procedure [47]. The results are related to the D65 illuminant and the CIE 1964 standard colorimetric observer (10° standard observer) [2].

The scale adjustment represents a very important step [48] and it was performed using the white calibration plate (CM-A145) as a target