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Study of color characteristics of pigments and paints by spectrophotometer

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Abstract. Nowadays, in restoring and examining paintings, the search for effective analytical methods for studying paint pigments is very actual. The identification of poor pigments is important itself, but it is also important for the determination of pigments in paints with different binders. Many studies were done in this field by means of Raman and IR Fourier spectroscopy, X-ray fluorescence spectrometry and some others. However, all the mentioned methods require the use of complex and expensive equipment, sampling, and preparation of samples. For this reason, the search for new simple non-destructive, and inexpensive testing methods is still very actual. In this work for studying color characteristics of pigments, the spectrophotometry method was used. In the experiments, the color characteristics of model samples were studied. It was shown that the color characteristics of pigments and paints, including, for example, whitewash (lead, zinc, and titanium), have characteristic individual values of the color coordinates $L^*a^*b^*$ that may be used for their identification.

Keywords: spectrophotometry, pigments, paints, color characteristics

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Исследование цветовых характеристик пигментов и красок с помощью спектрофотометра

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Аннотация. В настоящее время при реставрации и экспертизе картин очень актуален поиск эффективных аналитических методов изучения пигментов красок. Идентификация чистых пигментов важно само по себе, но также важно определение пигментов в красках с различным связующим. В данной предметной области было проведено много исследований с помощью методов рамановской и ИК-фурье-спектроскопии, рентгеновской флуоресцентной спектрометрии и некоторых других. Однако все упомянутые методы требуют использования сложного и дорогостоящего оборудования, отбора проб и подготовки образцов. По этой причине поиск новых простых, неразрушающих и недорогих методов контроля по-прежнему является актуальной задачей. В данной работе для изучения цветовых характеристик пигментов был использован метод спектрофотометрии, с помощью которого экспериментов были изучены цветовые характеристики модельных образцов пигментов красок. Было показано, что цветовые характеристики пигментов и красок, включая, например, белила (свинцовые, цинковые и титановые), имеют характерные индивидуальные значения цветовых координат *L**a**b**, что может быть использовано для их идентификации

Ключевые слова: спектрофотометрnz, пигменты, краски, картины, цветовые характеристики.

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Introduction

Preserving art and artifacts is crucial for our history. Spectrophotometry measures reflection at different wavelengths, helping identify pigments without sampling. Analyzing the unique shapes of the spectrum curve reveals the colorants and pigments present. Visual reflectance spectrum and colorimetric coordinates provide vital information. The CIELAB system is widely used for chromatic coordinates and color visualization.

The CIELAB system analyzes reflectance spectrum differences influenced by pigments. Factors like deterioration, material content, and particle size affect color measurements. This study focuses on spectral curve measurements within the visible spectrum to understand color perception. Colorimetry considers illuminants, observers, and CIE standards [1]. Spectral analysis and CIE colorimetric data are used in studying colored objects. This paper discusses color science applications, including monitoring material changes, yellowing, gloss, fading or darkening. The studyexplores challenges and approaches with new binder materials like glue dispersion K9 acrylic and modern restoration materials such as Loropal (carbamide ormaldehyde resin resistant to yellowing) and iridescent pigments. Color measurement helps to document the color palette of some objects, so that we can see any changes in color. Routinely, there is a focus on identifying the oldest pigments by different methods of analysis. A direct and rapid identification of the minerals contained in tiny samples can be achieved by vibration and spectroscopic techniques.

The CIE (Commission International de l'Eclairage) 1976 (*L**a**b**), or the CIE LAB system, is widely used for recording the chromatic coordinates. This system, referred to as colorimetry, is an effective tool for visualizing the color. The characteristics of a painted surface may have been found to be determined based on differences in reflectance spectrum, which is commonly characteristic of each pigment. Various possible factors, such as deterioration processes in the image area, materials content, surface hardness and particle size, can influence measurements of colors [2].

Color measurement helps to document the color palette of some objects, so that we can see any changes in color. Routinely, there is a focus on identifying the oldest pigments by different methods of analysis. A direct and rapid identification of the minerals contained in tiny samples can be achieved by vibration and spectroscopic techniques. Raman microscopy is a sensitive, nondestructive tool for the study of single grains in pigment samples and has been able to achieve some successful results [3-4]. In addition, a wide variety of advantages have been demonstrated when scanning electron microscopes are used to characterize painted objects. For pigment and microchemical analysis, we could use a scanned electron microscope that is able to identify morphologic microstructure features. Several studies were carried out on the importance of color measurements in terms of conservation of Cultural Heritage, with a view to determining whether they are relevant. Different art works of easel painting and murals have successfully been captured using colorimetry. Document, oil painting, wall art and stone structures [5]. Marchiafava et al. [6] have reported that measurement of color is useful 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).

Materials and Methods

To study the color characteristics of paint pigments, model samples were prepared, which represented the coloring of natural pigments. The model samples are pigment stains on sheets of paper about 2×2 cm in size, ground with various binders. In the experiments, both natural (yellow and red ochres, black ivory – production of Kremer Pigmente GmbH & Co. KG) and synthetic (various whitewash) pigments were used, as well as their mixtures. They have been rubbed with binders including traditional materials (for example, linen oil) and modern restoration ones (such as dispersion K9 acrylic–carbamide formaldehyde resin resistant to yellowing and used in restoration as a binder when tinting the loss of painting).

Since the properties of the paper itself can influence the color characteristics of pigments, careful paper selection was required. In particular, the paper should not contain excessive amounts of titanium, lead and zinc, since the presence of these chemical elements may subsequent influence of model samples, and therefore lead to inaccuracies in the analysis of their color. The fact is that some pigments (for example, titanium, lead and zinc white) contain them in their composition. For this reason, the paper used to create model samples underwent elemental analysis, which was performed using the X-ray fluorescence spectroscopy method. XRF spectrometric analyzer Niton XL3t GOLD + (Thermo Fisher, USA) was used.

Color measurements of model samples were carried out by means of spectrophotometer BYK Gardner Spectro-guide 45/0. In the CIE $L^*a^*b^*$ color system, color differences, and locations were determined based on L^*, a^*, and b^* color coordinates. The symbols represent the following: a^* for red-green, b^* for yellow-blue, and L^* for black-white ($L^* = 0$ for black, $L^* = 100$ for white). To assess the impact of changes in color tone, evaluations were conducted separately for red tone ($+a^*$), yellow tone ($+b^*$), and brightness value (L^*). In our study, D65^o illuminance was employed, representing daylight and encompassing the entire visual spectrum from around 400 nm to slightly over 700 nm of light. The chosen observer degree, 10^o, corresponds better with human color perception.

The next step, a insulating layer has been laid upon it before drying to form the protective coating which is essential for wrapping this paper up so that it stays for longer time. Then it was covered by the glue dispersion K9 acrylic, which has a good binding capacity and widely used because of its low surface contamination without ammonia, formaldehyde free.

When thinned, it is possible to achieve a very matte finish. Then the pigments" (French Ochre, lead white, zinc white, red pole, terra Ercolano red natural land Ercolano Ivory black), were applied on the covered paper, measurements were collected by the spectrophotometer on each paint moving within the 4 cm × 4 cm area.

Results and Discussion

The CIE $L^*a^*b^*$ values recorded on the studied paint samples are given in Table 1 and demonstrates the BYK elemental analysis obtained on the studied samples.

Table 1

Chromatic coordinates ($L^*a^*b^*$) recorded on the studied pigment samples mixed with K9

	L^*	a^*	b^*
zinc white	97.04	0.42	3.93
lead white	97.00	–0.22	2.61
Titanium white	97.02	–0.78	2.74
French Ochre	55.95	13.65	41.61
Black Ivory	6.61	0.55	1.22
Red Bole	33.32	22.65	22.07
Red Terra	40.50	36.21	35.35

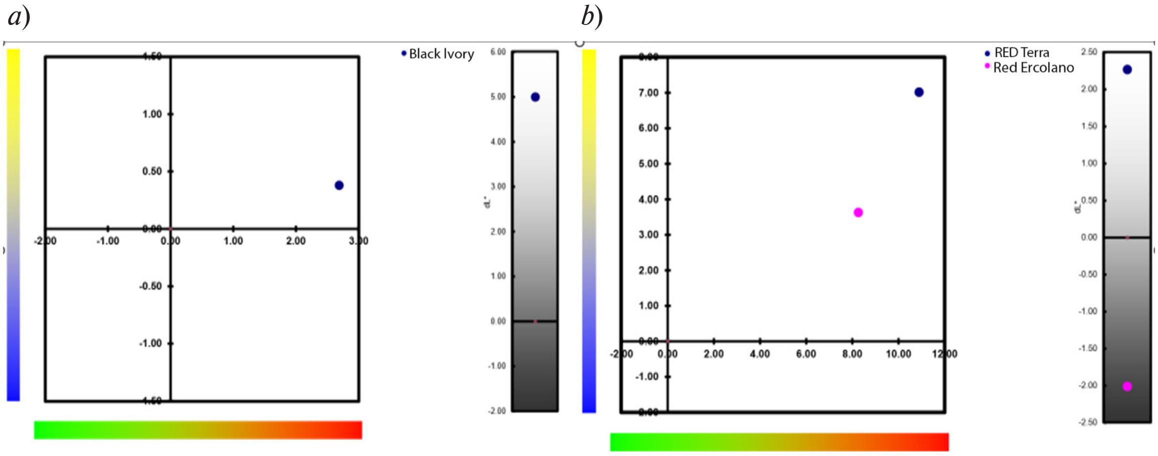

Fig. 1. CIELAB color differences (Δ*L**) (*a*); CIELAB color differences (Δ*L**, Δ*b**Δ*a**) Δ*a**, Δ*b**) for difference between the standard for the difference between the standard Red black and black ivory pole and red Terra Ercolano (*b*)

The dependence of Δ*b* versus Δ*a* is illustrated in Fig. 1,*a*. It is apparent that black ivory is redder than standard black. The color differences calculated for black ivory versus black as standard are from these values it can be seen that the major difference between these two blacks is in lighting (*L*). From graphing the chromaticity coordinates Fig. 1,*b* of the Red Terra Ercolano, with the standard “Red Pole”, the red Terra have determined that it is redder and more yellowness than the others, and the values of L indicate it is lighter than the other two reds pigments.

This paper substrate involves the main class color spaces, CIE *L***a***b** color space, which is recommended to use in the case of our study instead of LIELCH , and the reason is that *L***a***b** and LCH can both done manually, but it depends on which if you have chromatic or non-chromatic colors, so *L***a***b** usually used for colors that are under a chroma of 10 and anything over that we could use both LCH and *L***a***b**, so what it does because of the way the calculations are set up when you switch to LCH, some variations are gained on the chroma axis.

The plotted as percent reflectance on the vertical axis (*y*) versus wavelength on the horizontal axis (*x*) at a scale of 400-700 nm is presented with the used pigments (Fig. 2). Fig. 2,*a* shows the reflectance spectrum of the yellow French ochre pigment, which is mixed with K9 glue, the curve shape at 540–560 nm is characteristic of yellow paint which started to show high reflection intensity shoulders and above 560 nm, the chemical composition of this yellow is SiO_2, Al_2O_3, Fe_2O.The average values for *a** and *b** were (13.65) and (41.61), respectively. In terms of black pigment, a low reflectance intensity has been detected. The observation of the reflectance spectrum curve registered on the black pigment sample (Fig. 2,*b*) A slope on the wavelength of 400 nm was shown. Besides, there is a characteristic absorption band 420 nm was observed. The changes in the structure of the pigment and its composition are most likely to be the cause of this band. The closer a curve approaches this flat shape, the brighter it looks as neutral color and the lower its saturation or Chroma, which is Munsell’s designation that corresponds exactly to saturation. On the pigment, an *a** and *b** value of 0.58 was recorded. Both numbers are 0.55 and 1.22.

In addition to the positive *a** values, the microscopic observations showed that the sample tends towards yellow and red areas. In previous studies, the comparison of CIE *L***a***b** coordinates and reflection spectrum has allowed us to differentiate between standard black and Ivory Black. Conversely, the more contrast there is between the maximum and minimum reflectance, the higher is the saturation (Chroma), as seen in the reds pigments and, yellow, in Fig. 2,*a*,*c*, which is Red terra has the highest saturation (chroma) between the red. Fig. 3,*c* illustrates the spectrophotometric curves for reds, spectrum showed an increase at 560–700 nm (Fig. 2,*c*, *d*), and the band at 650 nm is for the Fe^{3+}absorption in red ochres, in Fig. 2,*e*. where each measurement was carried out three times with different surface homogeneity. Red bole is a natural, ferruginous aluminum silicate. It is similar to ochres in its chemical composition but is softer and more unctuous. The *a** and *b** average values for the red sample were (22.65) and (22.07) for the Red Bole, respectively and (36.21) and (35.35) for Red Terra and (34.80) and (32.17) for Red Ercolano.

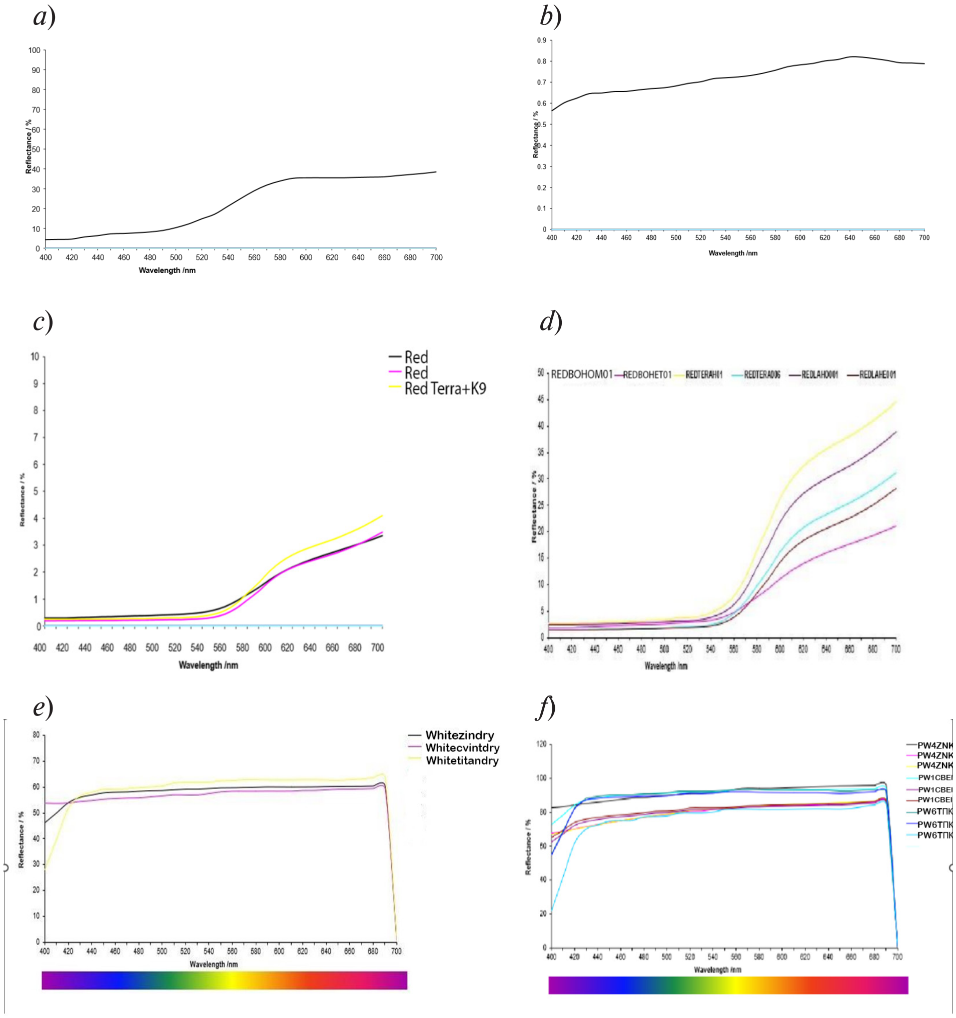

Fig. 2. Reflectance spectra of yellow French ochre pigments (mixed with glue K9) (*a*); reflectance spectra of Black ivory pigments (mixed with glue K9) (*b*); reflectance spectra of powders red pigments (red terra, ercolano land K9) (*c*); reflectance spectra of powders red pigments (red terra, Ercolano land) mixed with glue (*d*); reflectance spectra of powders white pigments (zinc-lead-tit) (*e*); reflectance spectra of powders white pigments mixed with K9 (zinc-lead-tit) (*f*)

Fig. 2, *e*, *f* shows the reflectance spectrum of the three white pigments(lead, zinc, and titanium), in Fig. 2,*f*, where each measurement was carried out three times with different surface homogeneity, the curve shape at beginning of the percent reflectance is characteristic of the titanium white pigment(PW6), in both dry and mixed with pure acrylic dispersion K9. The chromaticity coordinates (x, y) and the luminous reflectance, or lightness (L), of the three whites are given in Table 1. The L tristimulus value indicates that zinc white (PW4) is the lightest.

Conclusion

In conclusion, the interpretation of spectrophotometry reflectance curves in visible wavelengths serves a broader purpose beyond pigment identification. It encompasses a wide range of functions related to colors, making accurate interpretation of spectrophotometric data crucial.

By correctly interpreting such data, valuable assistance can be provided in identifying the pigments and paints used in paintings, enabling the implementation of optimal care and preservation methods. In the present study, both colorimetric and spectral reflectance analyses were conducted to examine the pigments. These analyses yield valuable information regarding the physical characteristics of cultural heritage objects, which can be documented through color documentation. To record color values, a BYK spectrophotometer was utilized, specifically capturing $L^*a^*b^*$ values.

This color space is typically employed for colors with a chroma below 10. Considering the chosen pigments and their chroma values, the use of $L^*a^*b^*$ calculations and coordinates proved to be the most suitable approach in our study. The investigation of the reflectance spectrum of the pigments played a significant role in their identification. This technique provides insights into the unique spectral characteristics exhibited by different pigments, aiding in their differentiation and classification.

Our future work will be focused on further optimizing, by looking at visible reflectance spectra of pigment powders to the ones of their mixed paints with the white pigments. In the case of red pigment containing zinc white and lead white pigments, this is intended to assess differences in reflectance spectrum which started at 30%, 50% and 70% respectively of percentage of the red pigment, also Controlling the homogeneity content of the pigment surface to be measured is important because homogeneity content does affect the pigments' spectral reflectance and (CIE $L^*a^*b^*$) values.

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